



US Army Corps
of Engineers
Construction Engineering
Research Laboratory

19990830 019

CERL Technical Report 99/71
August 1999

Reducing Air Pollutant Emissions From Solvent Multi-base Propellant Production

Michael R. Kemme and Michael Lateulere



Photocatalytic pollution control unit

The Radford Army Ammunition Plant, Virginia, is the multi-base propellant manufacturing facility for the Department of Defense. Solvent multi-base propellant production, however, emits large quantities of volatile organic compounds (VOCs). These VOC emissions are regulated under Title I of the Clean Air Act as precursors of tropospheric ozone. The pollutant stream also contains low concentrations of nitroglycerine (NG). The NG content prohibits the use of traditional air pollution control technologies because of safety concerns.

This report summarizes the research of CERL and others into alternative air pollution control

technologies. Bench-scale tests of sulfuric acid scrubbing, sorptive slurry biodegradation, and ultraviolet (UV) photocatalytic oxidation were conducted. The results of the UV photocatalytic oxidation tests showed the most promise based on safety, economic, and operational considerations and the remaining research effort focused on this technology.

UV photocatalytic oxidation was tested on a larger scale to determine its effectiveness. This report describes the results of the larger scale testing and presents a demonstration protocol that can be applied to future full-scale work.

Approved for public release; distribution is unlimited.

DTIC QUALITY INSPECTED 4

The contents of this report are not to be used for advertising, publication, or promotional purposes. Citation of trade names does not constitute an official endorsement or approval of the use of such commercial products. The findings of this report are not to be construed as an official Department of the Army position, unless so designated by other authorized documents.

DESTROY THIS REPORT WHEN IT IS NO LONGER NEEDED

DO NOT RETURN IT TO THE ORIGINATOR

USER EVALUATION OF REPORT

REFERENCE: CERL Technical Report 99/71, *Reducing Air Pollutant Emissions From Solvent Multi-base Propellant Production*

Please take a few minutes to answer the questions below, tear out this sheet, and return it to CERL. As user of this report, your customer comments will provide CERL with information essential for improving future reports.

1. Does this report satisfy a need? (Comment on purpose, related project, or other area of interest for which report will be used.)

2. How, specifically, is the report being used? (Information source, design data or procedure, management procedure, source of ideas, etc.)

3. Has the information in this report led to any quantitative savings as far as manhours/contract dollars saved, operating costs avoided, efficiencies achieved, etc.? If so, please elaborate.

4. What is your evaluation of this report in the following areas?

- a. Presentation: _____
- b. Completeness: _____
- c. Easy to Understand: _____
- d. Easy to Implement: _____
- e. Adequate Reference Material: _____
- f. Relates to Area of Interest: _____
- g. Did the report meet your expectations? _____
- h. Does the report raise unanswered questions? _____

- i. General Comments. (Indicate what you think should be changed to make this report and future reports of this type more responsive to your needs, more usable, improve readability, etc.)

5. If you would like to be contacted by the personnel who prepared this report to raise specific questions or discuss the topic, please fill in the following information.

Name:

Telephone Number:

Organization Address:

6. Please mail the completed form to:

Department of the Army
CONSTRUCTION ENGINEERING RESEARCH LABORATORY
ATTN: CEERD-IM-IT
P.O. Box 9005
Champaign, IL 61826-9005

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave Blank)		2. REPORT DATE August 1999		3. REPORT TYPE AND DATES COVERED Final	
4. TITLE AND SUBTITLE Reducing Air Pollutant Emissions From Solvent Multi-base Propellant Production				5. FUNDING NUMBERS 622720 D048 T27	
6. AUTHOR(S) Michael R. Kemme, Michael Lateulere, and Stephen W. Maloney					
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) U.S. Army Construction Engineering Research Laboratory (CERL) P.O. Box 9005 Champaign, IL 61826-9005				8. PERFORMING ORGANIZATION REPORT NUMBER TR 99/71	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Headquarters U.S. Army Corps of Engineers (HQUSACE) ATTN: CEMP 20 Massachusetts Ave., NW Washington, DC 20314-1000				10. SPONSORING / MONITORING AGENCY REPORT NUMBER	
9. SUPPLEMENTARY NOTES Copies are available from the National Technical Information Service, 5385 Port Royal Road, Springfield, VA 22161					
12a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.				12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) <p>The Radford Army Ammunition Plant, Virginia, is the multi-base propellant manufacturing facility for the Department of Defense (DoD). Solvent multi-base propellant production, however, emits large quantities of volatile organic compounds (VOCs). These VOC emissions are regulated under Title I of the Clean Air Act as precursors of tropospheric ozone. The pollutant stream also contains low concentrations of nitroglycerine (NG). The NG content prohibits the use of traditional air pollution control technologies because of safety concerns.</p> <p>This report summarizes the research of CERL and others into alternative air pollution control technologies. Bench-scale tests of sulfuric acid scrubbing, sorptive slurry biodegradation, and ultraviolet (UV) photocatalytic oxidation were conducted. The results of the UV photocatalytic oxidation tests showed the most promise based on safety, economic, and operational considerations and the remaining research effort focused on this technology.</p> <p>UV photocatalytic oxidation was tested on a larger scale to determine its effectiveness. This report describes the results of the larger scale testing and presents a demonstration protocol that can be applied to future full-scale work.</p>					
14. SUBJECT TERMS air pollution control technologies propellants pollution prevention solvents Radford Army Ammunition Plant volatile organic compounds (VOCs)				15. NUMBER OF PAGES 84	
				16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified		18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified		19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	
				20. LIMITATION OF ABSTRACT SAR	

Foreword

This study was conducted for the Directorate of Military Programs, Headquarters, U.S. Army Corps of Engineers (HQUSACE), under Project 622720048, "Industrial Operations Pollution Control"; Work Unit T27, "Abatement of VOCs from Solvent Multi-Base Propellant Production." The technical reviewer was James Small, U.S. Army Industrial Operations Command (AMSIO-IBR).

The work was performed by the Environmental Processes Branch (CN-E) of the Installations Division (CN), U.S. Army Construction Engineering Research Laboratory (CERL). The CERL principal investigator was Michael R. Kemme. L. Jerome Benson is Chief, CN-E, and Dr. John T. Bandy is Chief, CN. The technical editor was Linda L. Wheatley, Information Technology Laboratory.

Dr. Michael J. O'Connor is Director of CERL.

Contents

SF 298.....	1
Foreword.....	2
List of Figures.....	5
1 Introduction.....	7
Background.....	7
Objective.....	8
Approach.....	8
Mode of Technology Transfer.....	8
2 Description of Problem.....	10
Regulatory Issues.....	10
Description of the Solvent Multi-Base Propellant Manufacturing Process.....	11
Source Characterization.....	13
Safety Issues.....	16
3 Technologies Considered.....	17
Description of Available VOC Control Options.....	17
Economics of Traditional Control Technologies.....	20
Specific Technologies Studied.....	21
Comparison of Studied Technologies.....	25
4 UV Photocatalytic Oxidation.....	28
Technology Description.....	28
Conclusions From Earlier Work.....	33
Description of the 650 SCFM PPCU.....	41
5 Demonstration.....	49
Purpose.....	49
Equipment Setup for Demonstration.....	50
Parameters To Study.....	52
Test Plan.....	55
Demonstration Schedule.....	59

6	Conclusions	60
	Characterization of Emission Sources	60
	Bench Tests of Likely Technologies.....	61
	Development of Equipment and Testing Parameters.....	61
	References.....	62
	Appendix A: Risk Assessment of 650 SCFM Photocatalytic Pollution Control Unit	65
	Acronyms and Abbreviations	81
	Distribution	

List of Figures

1	Diagram of solvent multi-base propellant manufacturing process.....	12
2	Acetone and ethanol emissions from a full FAD bay	14
3	NG emissions from a full FAD bay (Bay 1) and a partially full bay (Bay 2)	14
4	Schematic diagram of the sorptive slurry bioscrubber	23
5	Schematic diagram of photoreactor experimental setup	24
6	Destruction of NG in a photoreactor	29
7	How titania-catalyzed photolysis works	30
8	Schematic diagram of the 5 SCFM UV photocatalytic reactor	34
9	Effect of space velocity in 5 SCFM reactor.....	35
10	DRE at several flow rates for one cell of the 50 SCFM PPCU	37
11	SCP 8 single cell photoreactor	39
12	Possible hydrogen bonding of titania particles to cellulose fibers	39
13	Summary of NG photocatalytic tests at Indian Head and FSEC.....	41
14	650 SCFM PPCU.....	42
15	Details of flow passage through FSEC's catalysts cartridge	43
16	Interior of a 650 SCFM PPCU module	44
17	Cross-section of the 650 SCFM PPCU module.....	45
18	650 SCFM PPCU equipment setup.....	50
19	Block diagram for NG continuous emission monitor	53

1 Introduction

Background

Organic solvents used in the manufacture of multi-base propellants are emitted to the atmosphere as volatile organic compounds (VOCs) from mixing rooms, propellant drying rooms, and other uncontrolled emission points. One of the solvents used is ethanol, which is regulated as a tropospheric ozone precursor. The inability to control ethanol emissions has resulted in the Commonwealth of Virginia Department of Environmental Quality (VDEQ) limiting production capability at Radford Army Ammunition Plant (RAAP), the sole active multi-base propellant manufacturing facility for the Department of Defense (DoD). The pollutant stream also contains low concentrations of nitroglycerine (NG), which prohibits using traditional air pollution control technologies because of safety concerns.

Much research has been conducted into RAAP's solvent multi-base VOC compliance problem in particular and the control of NG emissions in general. Before the U.S. Army Construction Engineering Research Laboratory (CERL) became involved, the Production Base Modernization Activity (PBMA), Picatinny Arsenal, NJ, sponsored research in this area. Some major research efforts sponsored by PBMA included a solvent multi-base emission characterization report (Hume and Worrell 1993), a study of sulfuric acid scrubbing (Liu, Hanesian, and Roche 1992), and initial research into ultraviolet (UV) photocatalysis (T-Raissi and Muradov 1992). The UV photocatalytic research was performed in partnership with the Indian Head Division of the Naval Surface Warfare Center (Indian Head, MD). Some of the results from these studies will be discussed in this report.

In fiscal year (FY) 1993, the research into this problem was transitioned to CERL. CERL continued its research partnership with Indian Head and the joint sponsorship of UV photocatalytic research performed by the Florida Solar Energy Center (FSEC), University of Central Florida, Cocoa, FL. The results of FSEC's research and other research performed by CERL will also be described in this report.

Objective

The objective of this research program was to develop technology to safely control emissions of organic pollutants created during the manufacture of solvent multi-base propellants. The research program was designed to characterize the emission sources, bench test likely control technologies, select the most promising technology for further testing, and develop information required for a demonstration of the selected technology.

Approach

The general approach for this research program consisted of the following steps:

1. Analyze existing emission studies and perform additional studies to fully characterize the important emission points in the solvent multi-base manufacturing process
2. Perform bench-scale studies for likely air pollutant removal technologies
3. Select the most promising pollutant removal technology for more detailed study
4. Develop hazard analysis and testing protocol information to aid in the demonstration of the selected pollutant control technology.

Mode of Technology Transfer

The primary purpose of this project was to develop a pollution control technology for solvent multi-base propellant production to the point where a large-scale demonstration of the technology in the field would be feasible. The information contained in this technical report will be used to plan and execute technology demonstrations. Two separate demonstration activities are planned.

In FY95 Indian Head began a project to demonstrate the control of NG emissions by UV photocatalysis. The project was funded through the Environmental Security Technology Certification Program (ESTCP). This project culminated in the demonstration of a 650 SCFM photocatalytic pollution control unit (PPCU) at Indian Head in 1998.

In FY98 CERL and MSE Technology Application, Inc. (MSE) began a project to demonstrate UV photocatalysis at RAAP. As planned, this project will use the same 650 SCFM PPCU built for the Indian Head project.

2 Description of Problem

Regulatory Issues

The pollution abatement requirements for the manufacture of solvent multi-base propellants were first examined in January 1975. At that time, the VDEQ studied imposition of air emission standards on this manufacturing process, which was a known source of VOC emissions. However, VDEQ found no proven methods of safely reducing the VOC emissions from the manufacture of solvent multi-base propellants. The use of traditional air pollution control equipment would have created an explosion hazard for the NG-laden gas stream.

In January 1980 RAAP's application for a permit to construct and operate the Continuous Automated Multi-Base Line facility was approved. As was the case in 1975, none of the existing air pollution control alternatives were considered safe. The VDEQ issued the construction permit with the following stipulations:

1. The construction and operation of the facility shall result in no net increase in VOC emissions from RAAP as a whole.
2. The plant shall continue to investigate methods of controlling VOC emissions and shall report annually on the results of these investigations beginning 1 July 1980.
3. Should a method of control for VOC emissions from the plant become feasible, RAAP shall install that equipment as soon as practical.
4. The board reserves the right to modify and, if appropriate, to reissue or rescind the permit.

The VDEQ has not imposed tougher VOC emission restrictions on the manufacture of multi-base propellant as yet, but could impose restrictions at any time. The recent removal of acetone from the list of VOCs in 1995, combined with the low production rate for these propellants, has eased the pressure. However, the VDEQ has been briefed annually on the progress made toward the development of a safe control technology. Since FY93, CERL has described the progress

achieved through the work completed during the research project. During these briefings, the VDEQ has clearly stated that progress must continue or other sanctions may be imposed at RAAP.

The Virginia air pollution control regulations contain a standard for NG as an air toxic. Based on their potential hourly and yearly NG emissions, RAAP would not be exempt from this regulation. The standard is based on allowable fence line ambient air concentrations of NG averaged over an hour and a year. However, the VDEQ has never required RAAP to determine if they are exceeding this standard. The VDEQ could require RAAP to perform air dispersion modeling studies to estimate fence line concentrations of NG emitted from all sources. If the modeling results showed concentrations exceeding the standard, then RAAP would be required to reduce NG emissions.

Description of the Solvent Multi-Base Propellant Manufacturing Process

RAAP manufactures many types of propellants, explosives, and pyrotechnics. Propellants are materials that very rapidly generate gas when ignited. Propellants are used to propel many objects including shells from guns, rockets, missiles, torpedoes, and pilot ejection seats.

Some propellants are manufactured using organic solvents while other propellants do not require the use of solvents. Propellants are further categorized based on their NG content. Single-base propellants do not contain NG, while multi-base propellants do contain NG. Since the emissions from solvent multi-base propellant manufacturing are the only emissions presenting a compliance problem to RAAP, the research project described in this report focused on this process.

Figure 1 depicts the solvent multi-base propellant manufacturing process. The propellant formulation and manufacturing process steps vary for each type of propellant being produced. Propellant production is a batch process consisting of the following sequential steps:

1. Nitrocellulose dehydration – Water is removed from nitrocellulose by adding ethanol and applying pressure with a ram press.
2. Block breaking – Pressed nitrocellulose is broken into pieces in the block breaker and placed into tubs.

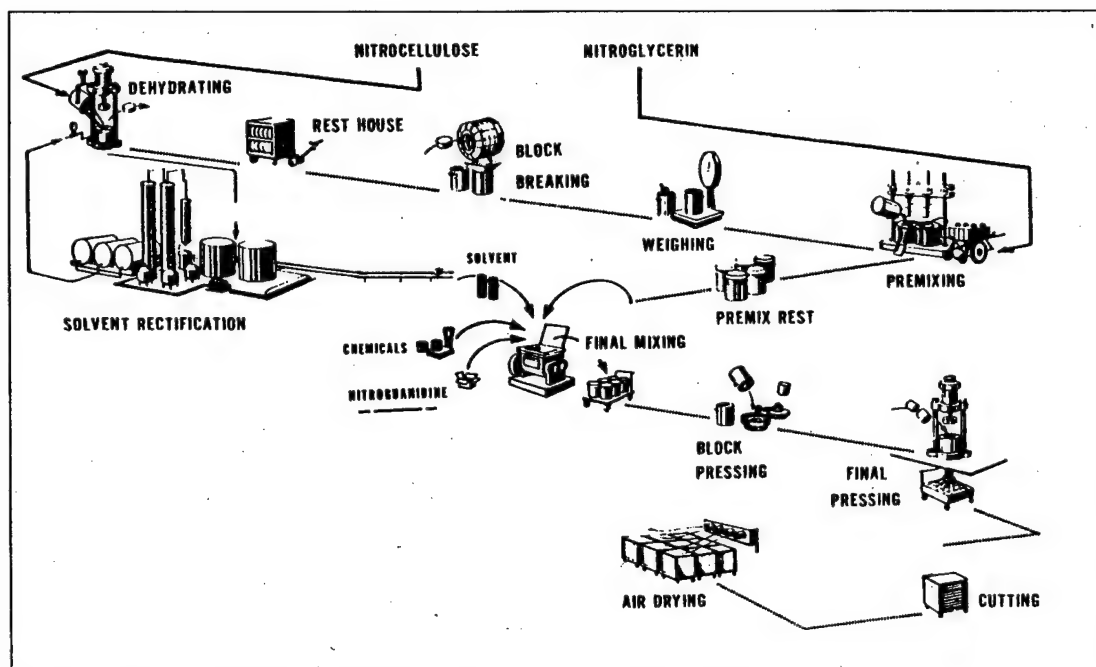


Figure 1. Diagram of solvent multi-base propellant manufacturing process.

3. Premixing – NG is mixed into the tubs of solvent wet nitrocellulose. The amount of NG will vary with the type of propellant being produced.
4. Final mixing – Nitrocellulose/NG, ethanol, acetone, and other additives are mixed in a large dough mixer for a prescribed time period. The amount of these ingredients will vary depending on the type of propellant being produced.
5. Dry down – At the end of the final mixing cycle, the mixer lid is opened and nitrogen gas is blown across the surface of the propellant. The nitrogen evaporates excess solvent until the propellant dough reaches the proper plasticity.
6. Blocking – Propellant dough is formed into blocks in a press.
7. Pressing – Blocked propellant is extruded to form strands of various shapes depending on the propellant being produced.
8. Boarding and cutting – Extruded propellant strands are cut to the proper length, placed onto boards, and the boards stacked in a cart.
9. Forced air dry (FAD) – Boarded propellant is placed into FAD bays where air is blown across the surface of the propellant. The FAD step dries the propellant and improves its mechanical properties. Some propellants have just a heating

cycle where the air temperature is ramped up over time to around 140 °F. Other propellants also include an ambient temperature cycle before the heating cycle. The propellant is left in the FAD bays for several days. The amount of time varies depending on the type of propellant.

Solvent multi-base propellant manufacturing has dropped significantly since the early 1980s. In 1984 RAAP produced about 23 million pounds of this propellant type. In recent years, RAAP has produced almost no solvent multi-base propellant. However, RAAP is expected to begin producing relatively large quantities of a new solvent multi-base propellant around the year 2000.

Source Characterization

To develop and design an air pollution control technology for the solvent multi-base propellant manufacturing process, the air emissions from the source must be characterized. Useful stream information includes the temperature, flow rate, and pollutant concentration. Studies performed by Hercules Inc. and by Roy F. Weston, Inc. provide the best information about emission streams from the solvent multi-base propellant manufacturing process (Hume and Worrell 1993; Roy F. Weston, Inc. 1998).

The study performed by Hercules Inc. combined a mass balance approach with air sampling to determine VOC emissions at every stage of the propellant production process. This study also included measurements of gas flow rate, temperature, and NG emissions from the FAD bays. M31A1E1 stick propellant for the 155-mm howitzer was the propellant produced during the test. This propellant was the major solvent multi-base propellant manufactured at the time.

The Hercules study concluded that approximately 65 percent of the VOC loss occurred during the mixing stage and 20 percent occurred at the FAD operation, for a total of about 85 percent of all VOC emissions from the manufacturing process. The emissions represented approximately 0.3 lb of solvent loss per pound of propellant produced. Figure 2 shows acetone and ethanol (alcohol) emissions over time from a full FAD bay. The concentration of solvents was highest at the start of the ambient cycle and was reduced over time. About 75 percent of the total solvent emissions occurred during the 45-hr ambient cycle. Granular propellants do not have an ambient cycle and solvent emissions from the FAD operation would likely have a higher concentration over a shorter time.

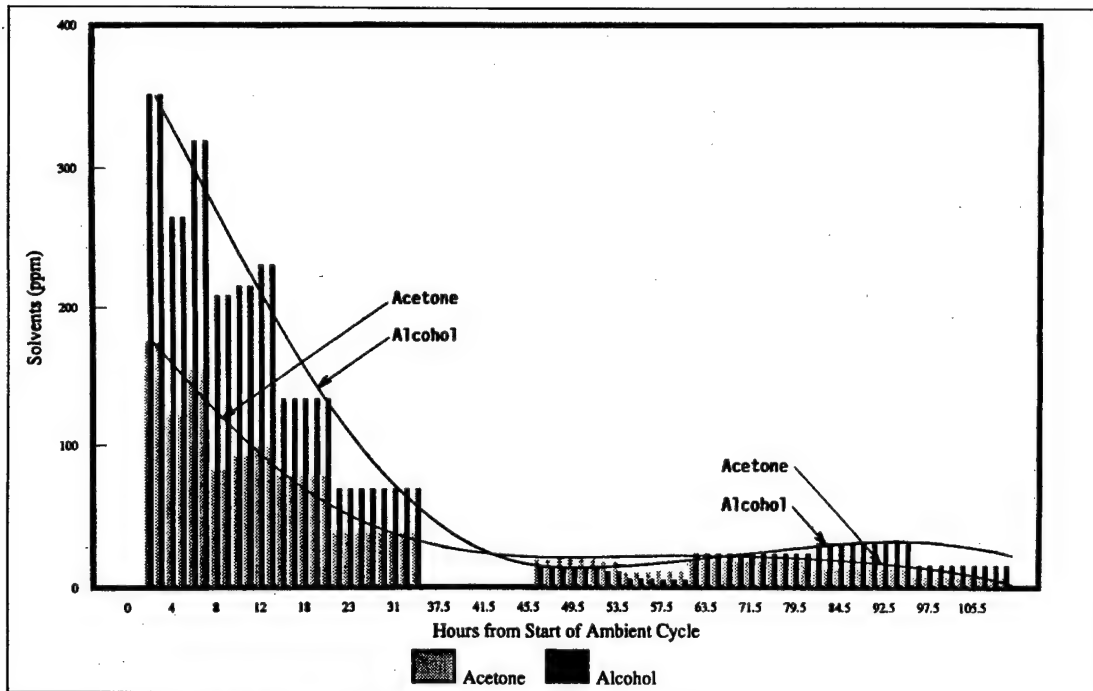


Figure 2. Acetone and ethanol emissions from a full FAD bay.

Figure 3 shows NG emissions over time from a full FAD bay and a partially full FAD bay. The concentration of NG was highest during the heating cycle. Granular propellants do not have an ambient cycle and NG emissions from the FAD operation would likely have a higher concentration over a shorter time.

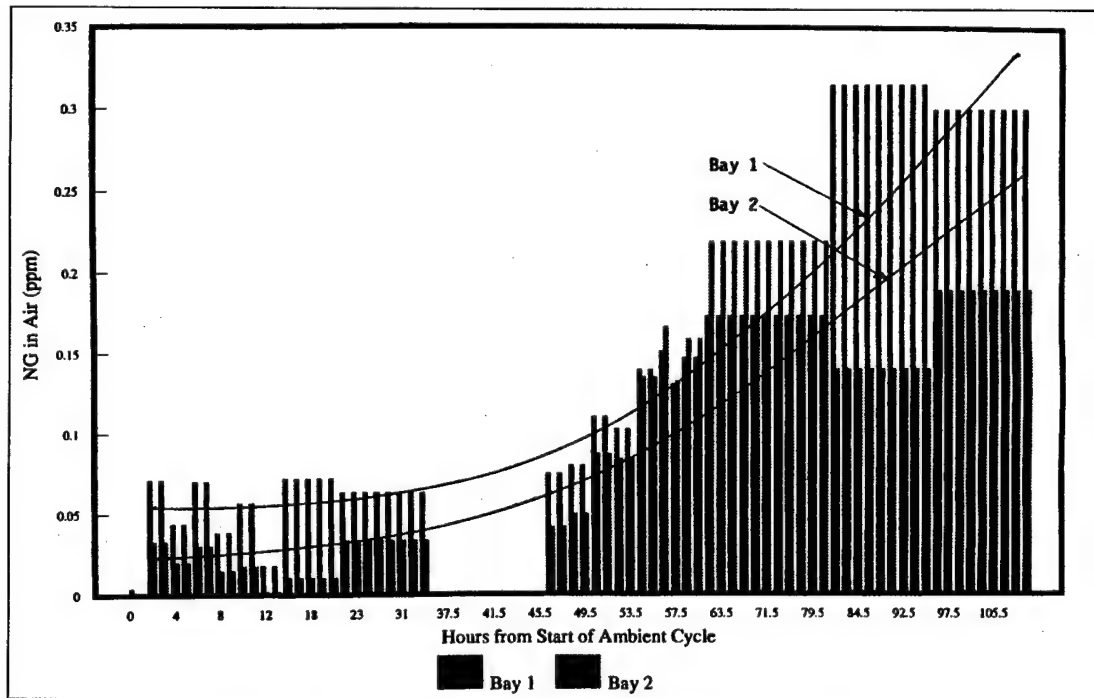


Figure 3. NG emissions from a full FAD bay (Bay 1) and a partially full bay (Bay 2).

Flow rates were measured for two FAD bays. Bay 1 had a flow rate of 5056 SCFM and Bay 2 had a flow rate of 4441 SCFM. The average flow rate from the two bays is 4748 SCFM. The maximum temperature of the air in the FAD was about 140 °F.

The Weston study performed was designed to provide more information about the mixing stage of the solvent multi-base propellant manufacturing process. The basic approach was to perform a "stack" test on the mixing room exhaust. The objective of the study was to characterize the NG emissions over the entire mixing stage and the acetone and ethanol emissions during the mixing cycle and during the dry down cycle. Gas flow rates through the mixing room were also determined.

The reported NG emissions were very low. The average NG concentration from all tests was 0.658 parts per billion by volume (ppbv) with a maximum concentration of 1.468 ppbv. The average mass flow rate for NG was 4.98×10^{-5} lb/hr with a maximum mass flow rate of 1.11×10^{-4} lb/hr. The concentration of NG should be much lower during the mixing stage than it is during the FAD since the temperatures are lower, the lid of the mixer is closed for most of the mixing cycle, there is more air flow per weight of propellant (about 2.9 SCFM/lb at mixer, 0.59 SCFM/lb at full FAD bay), and the exposed surface area is lower.

Unfortunately a laboratory error prevented the development of meaningful data for acetone and ethanol emissions. A permeable membrane dryer apparently removed a large portion of the acetone and ethanol from the collected gas sample. Because of this problem, the laboratory did not detect ethanol in a quality control sample containing 25 parts per million by volume (ppmv) ethanol.

The Weston study reported an average flow rate of 2,146 SCFM through the mixing rooms. This information combined with the mass loss information presented in the Hercules report allows the calculation of theoretical acetone and ethanol concentrations from the mixing room. The mass balance study reported about a 39.46 lb/mix loss of acetone and a 48.97 lb/mix loss of ethanol. The study also reported that about 75 percent of the emissions occurred during the dry down period. The dry down would then account for 29.6 lb/mix loss of acetone and 36.7 lb/mix loss of ethanol. If a 3.5-hr mixing cycle is assumed, the emission rate is 11.27 lb/hr for acetone and 13.99 lb/hr for ethanol. The calculated concentrations are 513 ppmv for acetone and 804 ppmv for ethanol over the entire mixing cycle. If a 15-min dry down is assumed, the emission rate is 118.4 lb/hr for acetone and 146.8 lb/hr for ethanol. The calculated concentrations are 5,390 ppmv for acetone and 8,440 ppmv for ethanol over the dry down period.

The dry down concentration will likely be significantly lower than this figure because of inefficiencies in the mixing room's vapor collection system. The 75 percent emission loss attributed to the dry down period also included losses that occurred when the mixers were unloaded.

Safety Issues

RAAP has not controlled VOC emissions from the solvent multi-base propellant manufacturing process because of the presence of NG in the waste gas streams. Liquid NG is a very powerful explosive that is very easily detonated through shock, electrical discharge, or reactions with other materials. The NG vapor found in the waste gas streams is not an explosion hazard.

Any air pollution control device must meet the following safety criteria:

- Prevent condensation or concentration of NG vapor
- Manufactured of materials that do not react with NG
- Prevent spark generation from metal to metal contact or discharge of static electricity
- No open flame or high temperature surfaces.

The single-base propellant line has been controlled for decades by an activated carbon adsorption system. Since the activated carbon beds concentrate NG and react with NG, this control technology is considered unsafe for use on the multi-base lines. Tests conducted with NG on activated carbon showed that the two are not compatible (Langford, Todd, and Price 1983). These tests indicated that NG loading on carbon could be as high as 10 percent. The study did not specifically state whether or not an explosion hazard existed, but it did state that the decomposition of NG was uncontrollable and NG adsorbed on activated carbon was in a continual state of decomposition, even at ambient temperatures.

3 Technologies Considered

Description of Available VOC Control Options

Traditional air pollution control for organic air pollutant streams can be divided into devices that use absorption, adsorption, condensation, and thermal oxidation. A nontraditional air pollution control technology that is becoming more commonplace is the use of biofilm reactors. The following sections briefly describe the operation of these air pollution control techniques and the safety issues associated with using them to control the multi-base waste gas streams at RAAP.

Absorption

Absorption refers to the intimate contact of gases with a liquid so that part of the gas stream is dissolved in the liquid. Air pollution control devices using absorption are known as wet scrubbers. A wet scrubber normally contains plates or packing material to allow the scrubbing liquid to come into close contact with the gas stream. The liquid and gas stream most often flow in countercurrent directions. As gases are dissolved into the scrubbing liquid, it begins to lose its ability to capture the gaseous contaminant. Therefore, a portion of the scrubbing liquid is normally wasted and replaced with virgin material.

This type of control technology could potentially be applied safely to the waste gas streams from the solvent multi-base manufacturing at RAAP. The NG removed from the gas stream would be dissolved in the scrubbing liquid and should no longer pose a threat. However, the absorption unit would need to be carefully designed so that NG would not condense on any solid surfaces cooled by the evaporation of the scrubbing liquid.

Adsorption

Adsorption is the process where one substance (the adsorbate) becomes concentrated on the surface of another substance (the adsorbent), which is usually a solid. Certain materials make better adsorbents than others do. The most

common adsorbents are activated carbon, activated alumina, silica gel, and zeolites. Activated carbon and zeolites are the most common adsorbents for the reduction of VOCs. As more gas is adsorbed onto the surface of an adsorbent, it begins to lose its ability to capture more of the air contaminant. Air pollution control devices using adsorption must either replace the adsorbent occasionally or regenerate the adsorbent using heat or steam. If an adsorbent is regenerated, the adsorbed gases must either be recovered or destroyed.

Adsorption is not a safe alternative for the multi-base waste gas streams at RAAP. NG will condense and be concentrated in the adsorbent. While in contact with the waste gas stream, the adsorbent would concentrate liquid NG to a point where an explosion hazard might exist. As mentioned in Chapter 2, tests conducted with NG on activated carbon have shown that NG loading on activated carbon can approach 10 percent and that the NG collected on the activated carbon decomposes in an exothermic reaction (Langford, Todd, and Price 1983).

Condensation

Condensation is the process of converting a gas to a liquid either by lowering its temperature or increasing its pressure. An air pollution control device using condensation is called a condenser. Most condensers cool gas streams rather than raising their pressure since increasing gas pressure can be expensive. Condensers cool gas streams either by direct contact with a coolant or by indirect contact where a surface separates the coolant from the gas stream. Condensers are often used when recovery of the air pollutant is desired.

Condensation is not a safe alternative for the multi-base waste gas streams at RAAP. By design, a condenser would condense NG to remove it from the gas stream. The liquid NG would pose an extreme safety hazard.

Thermal Oxidation

Thermal oxidation is the process of oxidizing VOCs to carbon dioxide (CO₂) and water vapor through combustion. Sufficient time, temperature, and turbulence are required to completely oxidize organic air pollutants. All VOCs will have a heat content and contribute toward their own combustion. However, additional heat must usually be applied to the waste gas stream to allow combustion to occur.

Thermal oxidation control devices can be categorized as flares, thermal incinerators, and catalytic incinerators. A flare directly combusts the air and organic pollutants at a burner without a reaction chamber. A thermal incinerator passes the waste gas stream into a reaction chamber that has been heated to a sufficient temperature to allow oxidation to occur. A catalytic incinerator is similar to a thermal incinerator. The difference is that the gases pass through a catalyst bed, which promotes oxidation at lower temperatures.

Thermal oxidation devices are not ideally suited to the multi-base waste gas streams at RAAP. These control devices do have the advantage of not collecting or condensing NG. However, any device with an open flame or elevated temperature is a cause for concern at a plant manufacturing explosives and propellants.

Biofilm Reactors

Besides the traditional physical-chemical methods of cleaning waste gases, biofilm reactors have also been used effectively to treat VOCs. The reactors completely mineralize the contaminants to CO₂, water, and biomass and work best at low gaseous concentrations (Ottengraf and Diks 1990). The three types of biofilm reactors currently being used are biofilters, fixed-film bioscrubbers, and suspended-growth bioscrubbers (Overcamp, Chang, and Grady 1993).

A *biofilter* is typically a large filter bed packed with material such as compost, peat, or soil that provides a large surface area for microbial growth. The media, surrounded by a wet biofilm, provide the biomass with essential inorganic nutrients. Both the aqueous phase and the microorganisms are stationary. Contaminated gas is slowly forced through the filter bed, and pollutants are continually sorbed to the biofilm and the medium and biodegraded.

Fixed-film bioscrubbers, similar to trickling filters used in wastewater treatment, consist of scrubbers packed with stationary support medium. Recirculating nutrient liquid enters from the top of the column to absorb the gaseous impurities and wets the biofilm on the support media. The gas flow can be co-current or countercurrent relative to the liquid flow. Contaminants sorb into the liquid, and are degraded in the biofilm.

Suspended-growth bioscrubbers are different from traditional biofilters and fixed-film systems in that both the microorganisms and liquid are mobile. Such a bioscrubber consists of a scrubbing column for absorption of the pollutant and an oxidation reactor for pollutant degradation and microorganism growth. The

biomass slurry is continually circulated between the two units. The absorption unit is a column bringing the liquid and gas into intimate contact, usually by countercurrent flow. Soluble gaseous contaminants are absorbed into the scrubbing liquid in the absorption unit. After flowing through the absorber, the liquid returns to the oxidation tank, where the majority of the contaminant degradation and microorganism growth takes place. In the oxidation reactor, mixing is provided by aeration and/or mechanical stirring to maintain the biomass in uniform suspension and to transfer oxygen to the liquid phase. Physical, chemical, and biological parameters (e.g., temperature, pH, dissolved oxygen level, inorganic nutrient concentration, mixing intensity, biomass concentration, and wastage rate) can be controlled in the oxidation reactor.

The safety issue associated with the use of biofilm reactors is unknown. NG would likely both absorb and adsorb onto the biofilm surface or its support. If the rate of NG accumulation exceeded the rate of NG biodegradation, an explosion could occur. Other solid surfaces within the reactor would also be potential sites for NG condensation.

Economics of Traditional Control Technologies

CERL funded an economic study by Dames and Moore (1995) to evaluate commercially available technologies for the control or recovery of acetone and ethanol at both the mixing room and FAD operation. This study assumed that NG had already been selectively removed from the gas stream. It also used data provided by vendors for economic information. The results of this study represent the contractor's opinion about technologies to control acetone and ethanol after another technology had selectively removed NG.

The study included the following pollution control methods:

- Solvent Recovery Methods
 - Condensation (water-based and cryogenic)
 - Carbon adsorption
 - Synthetic adsorption

- VOC Control Methods
 - Condensation
 - Adsorption
 - Absorption
 - Thermal incineration
 - Catalytic incineration.

A screening of these methods eliminated a few as inappropriate for the waste gas streams at the mixing room and FAD operation. At the mixing room, cryogenic condensation, all types of adsorption, thermal oxidation, and biofiltration were eliminated. At the FAD operation, all types of condensation, absorption, and thermal oxidation were eliminated.

At the mixing room, the Dames and Moore study ranked water-based condensation/absorption first followed by catalytic oxidation. The recovery of acetone and ethanol was shown to be economical although the cost to separate the acetone and ethanol from the water was not included in the estimated costs. At the FAD, pollution control methods were ranked in the following order: catalytic oxidation, biofiltration, zeolite adsorption, polymer adsorption, and synthetic adsorption.

Specific Technologies Studied

Three technologies were studied during this research program: sulfuric acid scrubbing, bioscrubbing, and UV photocatalytic oxidation. These technologies were selected based on their potential for safe control of the multi-base waste gas streams at RAAP.

New Jersey Institute of Technology (NJIT) Sulfuric Acid Scrubbing Studies

PBMA funded research by NJIT to study the use of high concentration sulfuric acid in a recirculating absorption packed tower (Liu, Hanesian, and Roche 1992). Vapor-liquid equilibrium (VLE) data were measured for acetone, ethanol, and diethyl ether using from 73 to 96 weight percent sulfuric acid. NJIT performed absorption studies with a 2-in. diameter tower packed to a height of 18 in. with ¼-in. Raschig rings.

The VLE data showed that concentrated sulfuric acid is an efficient absorbent for these organic compounds and that the sulfuric acid also reacts with the organic compounds. The VLE data also showed that Henry's Law* applied for lower concentrations of the solvents but did not apply at higher concentrations. The absorption studies showed that acetone would break through (defined as 85 percent VOC removal) in 4 to 5 hr for 76 percent acid but no breakthrough occurred after 24 hr for 96 percent acid. No breakthrough occurred for ethanol or diethyl ether in any of the experimental runs. Acid purging prolonged breakthrough for acetone. For 76 percent acid, the breakthrough occurred in about 21 hr for a purge rate of about 1 percent of the recirculation rate.

Humidity in the air had a pronounced weakening effect on sulfuric acid concentrations over time. The data show that, after 12 hr, 96 percent sulfuric acid is reduced to 89 percent and 76 percent sulfuric acid is reduced to 69 percent. These data are for no recirculation. The laboratory air humidity was not recorded.

Clemson Bioscrubber Studies

CERL funded preliminary research at Clemson University to study the potential of an innovative sorptive slurry bioscrubber. The sorptive slurry bioscrubber could potentially be used to treat waste gas before or after the NG was removed. However, the Clemson work focused on the treatment of gas streams without NG. Three reports and a thesis present the results of this work (Overcamp et al. 1994; Overcamp et al. 1995; Overcamp et al. 1996; Hammervold 1995).

A sorptive slurry bioscrubber combines powdered activated carbon with a suspended-growth bioscrubber to produce a control technology that can absorb, adsorb, and biodegrade pollutants from contaminated air streams. The addition of activated carbon allows increased pollutant removal from the gas phase due to adsorption on the carbon's large surface area and the carbon's affinity for organic compounds. The carbon was bioregenerated in the oxidation reactor.

A three-stage, conventional bioscrubber was tested in four types of experiments. Figure 4 shows a diagram of the bioscrubber. Gas-phase acetone concentrations of 10, 50, and 100 ppmv were tested at an air flow rate of 0.75 m³/min. Acetone

* Henry's Law states that, at a given temperature, the solubility of a gas in a liquid is directly proportional to the pressure of the gas above the liquid.

was chosen as the target compound for this work since it is less water soluble than ethanol, therefore presenting a greater challenge for the bioscrubber. The first set of experiments examined the ability of the system to absorb acetone in the column with a once-through flow of both distilled water and a mineral salts solution. Two liquid flow rates for each solution were tested to determine the effect of liquid flow rate. Next, experiments with two powdered activated-carbon concentrations in the mineral salts solution tested the additional removal of acetone by adsorption in a once-through flow in the column. A third set of experiments was conducted using the enriched biomass culture in the bioscrubber at steady-state conditions to determine the baseline removal for acetone. Lastly, powdered activated carbon was added to the bacterial slurry at an acetone concentration of 50 ppmv to measure the steady-state efficiency of the system.

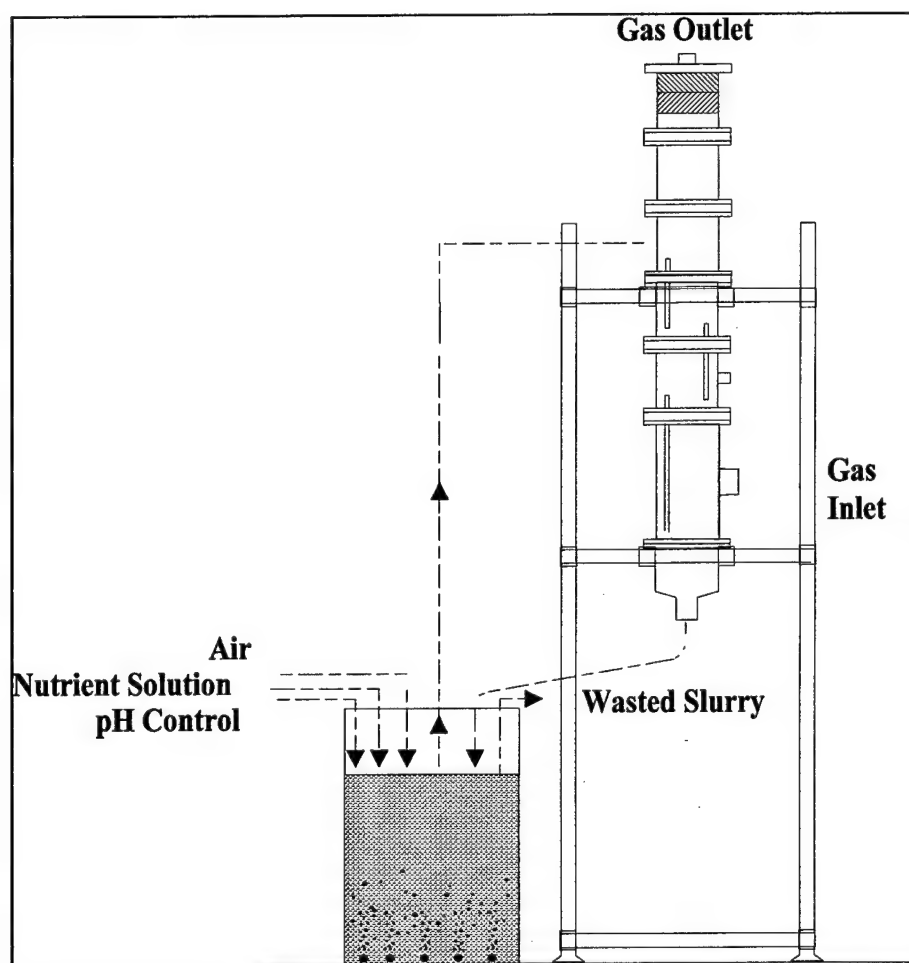


Figure 4. Schematic diagram of the sorptive slurry bioscrubber.

The experiments showed that the addition of powdered activated carbon improved the removal efficiency of the system and that the carbon was bioregenerated. At 50-ppmv inlet acetone concentration, the steady-state biological slurry in the bioscrubber removed 88 percent of the acetone. The removal efficiency increased to 93 percent when activated carbon was added to the system. The theory of adding activated carbon to increase gaseous pollutant removal in a bioscrubber has thus been supported by data on the control of acetone.

Florida Solar Energy Center UV Photocatalytic Studies

Indian Head, PBMA, and CERL funded FSEC to study the use of UV photocatalysis as a potential removal mechanism for emissions from the multi-base propellant manufacturing processes at Indian Head and RAAP. Both basic and applied research were conducted during this study. The basic research focused on determining half-cell reactions on the semiconductor surface involving NG and several electrolytes. This research also included work to determine the redox potential of several nitrate esters (e.g., NG). The applied research involved the design, fabrication, and evaluation of several catalytic and noncatalytic photoreactors. Two photoreactor designs were developed and tested. Reactor capacity and throughput varied in the range of 0.012 to 0.45 cu ft (0.33 to 12.8 liters) and 3.5×10^{-3} to 0.99 SCFM (0.1 to 28 lpm). Figure 5 shows the experimental setup for the smaller of the two reactor designs. NG inlet concentrations varied from 1.0 to 74.0 ppmv, while ethanol and acetone inlet concentrations were held steady at 900 ppmv and 450 ppmv, respectively.

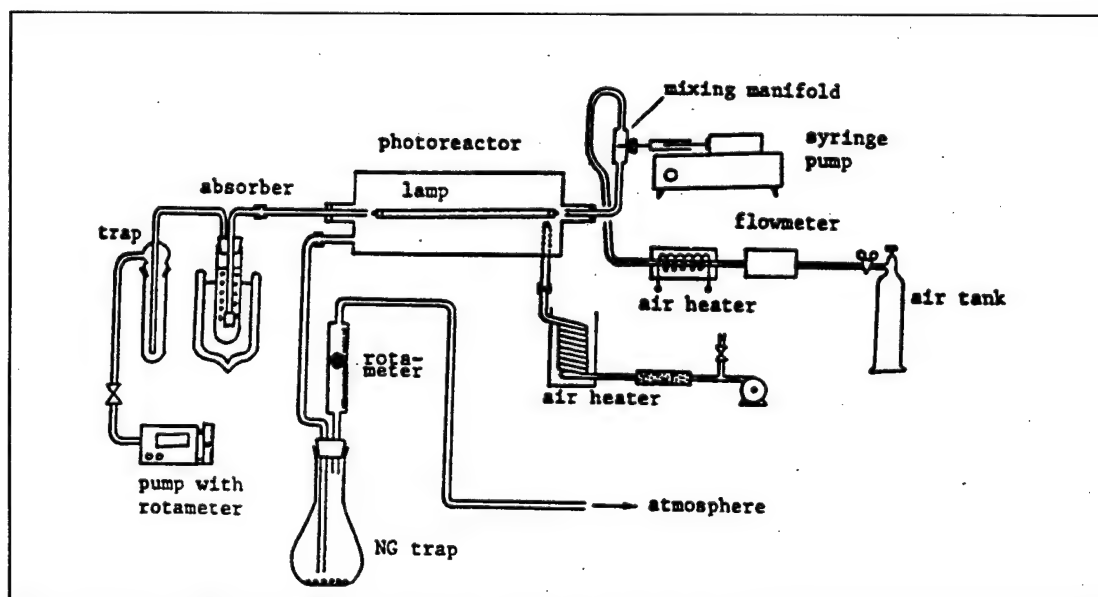


Figure 5. Schematic diagram of photoreactor experimental setup.

FSEC researchers reached the following conclusions:

1. The basic research effort discovered that irradiated titanium dioxide (TiO_2) is energetically capable of both oxidizing and reducing NG.
2. The photocatalytic decomposition of NG and VOCs was very efficient. It was possible to reduce the levels of all contaminants below 0.1 ppmv in a single pass through the photoreactor.
3. The presence of oxygen dramatically increased the destruction efficiencies and rates in the photoreactor. This effect was attributed to the generation of ozone in the photoreactor.
4. The addition of water vapor markedly increased the efficiency of NG, ethanol, and acetone photodegradation.
5. The rate of NG adsorption onto the catalyst surface had a negligible effect when compared to the photodecomposition on the catalyst surface.
6. TiO_2 had the highest activity for NG destruction compared to any of the other photocatalyst investigated.
7. NO_2 was the main nitrogen-containing product of NG photodestruction.
8. A potential exists for selective destruction of NG in mixed gas streams.

Comparison of Studied Technologies

The following criteria were used to select one of the three studied technologies for further development:

- Safety – Avoid condensation/concentration and open flame/high temperature
- Ability to operate intermittently with long down periods
- Production of waste streams
- Selective destruction of NG.

Sorptive Slurry Bioscrubber or Other Biofilm Reactors

Advantages:

- Does not generate any other waste streams since it completely mineralizes pollutants in the biofilm.

Disadvantages:

- Unknown if safe operation is possible
- Cannot operate intermittently with long down times without taking steps to keep the biofilm active
- Cannot selectively remove NG from gas streams.

The unknown safety issues and the inability to handle intermittent batch operations are the biggest disadvantages to this technology. Further work could determine associated safety issues. However, unless the production of solvent multi-base propellant greatly increases and stabilizes, this technology will never be a viable option.

Sulfuric Acid Scrubbing

Advantages:

- With the proper design, safe operation should be achievable
- Can operate with long down times.

Disadvantages:

- The wasted sulfuric acid scrubbing liquid is a hazardous waste
- Cannot selectively remove NG from gas streams.

Since this technology is capable of safe operation and intermittent operation, it does have some potential as a control device for the solvent multi-base line. However, the production of sulfuric acid-based hazardous waste would make the operation of the scrubber expensive.

UV Photocatalytic Oxidation

Advantages:

- With the proper design, safe operation should be achievable
- Can operate with long down times
- Does not produce other waste streams
- Can potentially remove NG from waste gas stream selectively.

Because of its inherent advantages, UV photocatalytic oxidation was selected for further development. Chapter 4 provides more details about how the technology works and describes the work performed to further develop the technology.

4 UV Photocatalytic Oxidation

Technology Description

Advanced oxidation technologies have been defined by Glaze (1994) as near ambient temperature processes that involve the generation of highly reactive radical intermediates, especially the hydroxyl radical ($\bullet\text{OH}$). One of the advanced oxidation technologies, which Glaze discusses, is heterogeneous photocatalysis. Photocatalytic oxidation of organic molecules is a process that uses UV light and a semiconductor photocatalyst to generate highly reactive species, among which are hydroxyl ($\bullet\text{OH}$), peroxy ($\text{HO}_2\bullet$) and superoxide ion ($\text{O}_2^{\bullet-}$) radicals. The hydroxyl radical is able to attack virtually any organic compound. Hydroxyl radicals typically react 1 million to 1 billion times faster than other common oxidizing agents such as ozone (O_3) and hydrogen peroxide (H_2O_2). If the reaction proceeds to completion, the organic compound is said to be mineralized. In the case of NG mineralization, the products are CO_2 , water (H_2O), nitric oxide (NO), nitrogen dioxide (NO_2), and nitric acid (HNO_3). The process by which organic contaminants are destroyed using heterogeneous photocatalysis can be described in these seven steps:

1. catalyst photo-activation
2. generation of active radicals
3. diffusion of the organic compounds through the bulk medium to the catalyst surface
4. adsorption of the compounds onto the catalyst surface
5. reaction of the compounds with reactive radicals
6. desorption of the reaction products from the catalyst surface
7. diffusion of the reaction products into the bulk media.

This description ignores photolytic reactions in which target compounds are mineralized by direct reactions with UV photons, as well as oxidation of target compounds by direct reactions with the oxidants. It is difficult to isolate the effect of these reactions on the reaction rate of organic compound decomposition, but their contribution should be minor in compared with heterogeneous photocatalysis. All reaction routes are depicted in Figure 6.

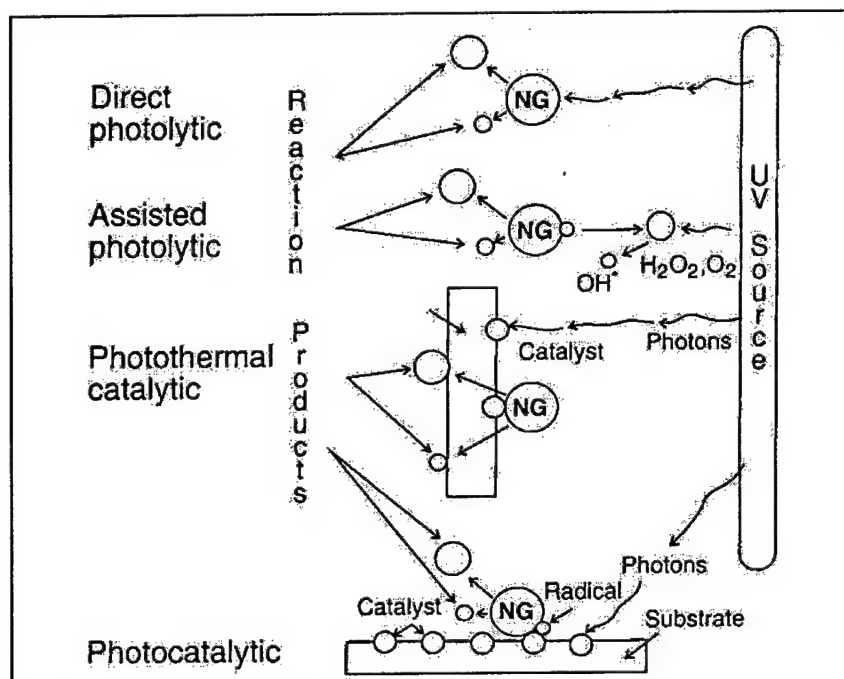
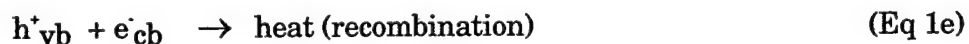
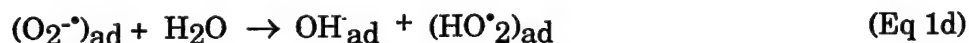


Figure 6. Destruction of NG in a photoreactor.

Photocatalytic activation leading to the generation of active radicals can be described by the following reactions:



The first step of this process occurs in the TiO_2 lattice and is described by equation 1a (T-Raissi et al., September 1997). When TiO_2 absorbs a UV photon

(represented by $h\nu$) having an energy equal to or greater than its bandgap energy, electrons (e_{cb}^-) shift to the conduction band, and positively charged "holes" (h_{vb}^+) are created in the valence band. Energy is related to wavelength by Planck's equation:

$$E = \frac{hc}{\lambda} \quad (\text{Eq 2})$$

where: E = bandgap energy (eV)

h = Planck's constant (6.6256×10^{-34} Js)

c = velocity of light (2.998×10^{10} cm/s)

λ = wavelength (nanometers)

With this equation one can calculate the longest wavelength needed to excite TiO_2 catalyst. Using the bandgap energy for TiO_2 of 3.1 eV, it is found that the threshold wavelength is 400 nm. TiO_2 will absorb light having a wavelength equal to or lower than this value.

Once the holes and the electrons are photogenerated, they are free to move about the crystal lattice. They either recombine (thermalize) per equation 1e or reach the surface of the catalyst to react with adsorbed species and produce reactive radicals per equations 1b - 1d (as illustrated in Figure 7).

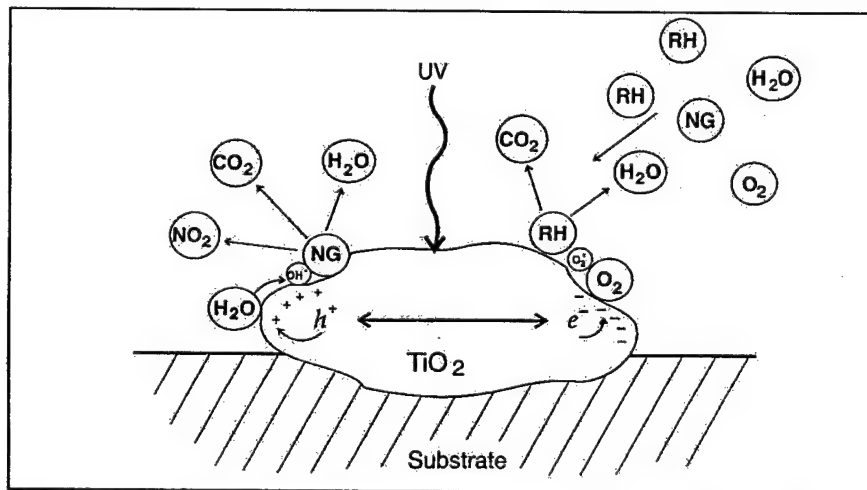
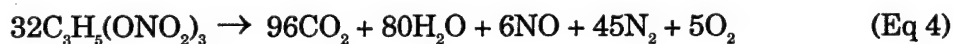
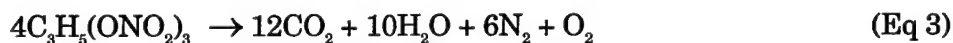


Figure 7. How titania-catalyzed photolysis works.

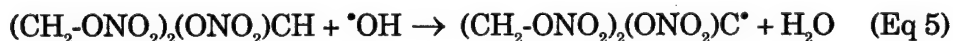
The rate of recombination of holes and electrons is a function of the catalyst surface irradiance. The higher the surface irradiance the greater the rate of recombination. It is critical to minimize the rate of recombination in order to maximize the reaction efficiency and ultimately reduce the cost of the technology. Researchers have found a threshold value of surface irradiance at which the dependence of the reaction rate on the surface irradiance transitions from a linear behavior to a square root behavior. Known as the Egerton-King threshold, knowledge of it is used to design efficient reactors.

Unless accounted for, the mass transfer step of heterogeneous photocatalysis limits the process. If organic compound molecules do not contact the catalyst, the reaction cannot occur. For waste streams with very low concentration of contaminants, the effect of diffusion becomes more pronounced. UV photocatalytic reactors must be designed to maximize contact between the organic compounds to be mineralized and the photocatalyst. Once organic compounds contact TiO_2 , they can react with the reactive radicals on the surface of the catalyst.

Virtually no data can be found on the photolysis or photocatalysis of nitrate esters and, particularly, NG. It is known that NG is subject to two types of decomposition: explosive (equation 3) and slow (or low temperature) (equation 4) (Urbanski 1965).



In photocatalytic experiments using annular photoreactors (volume < 1 L), it was found that more than 95 percent of NG nitrogen entering the photoreactor was converted into NO, NO_2 , and HNO_3 . Based on the data from DR-FTIR* measurements and continuous flow experiments, Muradov et al. (1997) proposed that, in all likelihood, the first step during NG photocatalytic (TiO_2) decomposition involves attack of the weak (tertiary) C-H bond in the NG molecule by photo-generated species (most importantly the OH radical):



* DR-FTIR = diffuse reflectance Fourier-transform infrared

The resulting radical is unstable and decomposes yielding a number of intermediate radicals and unstable compounds, which in the presence of oxidizers ($\cdot\text{OH}$, $\cdot\text{O}_2\text{H}$, O_3 , O_2) produce final products of NG oxidative destruction:



where: O_x = oxidizer

$\text{R}_1(\text{ONO}_2)_n$ = nitrate group containing radicals and unstable products (e.g., $\cdot\text{CH}_2\text{ONO}_2$, mono- and dinitroglycerin, etc.)

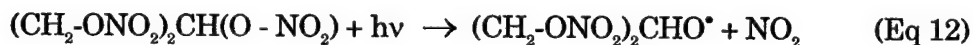
R_2OH = radicals and easily oxidizable products (e.g., $\cdot\text{CHO}$, CH_2O , $\cdot\text{C}_2\text{H}_3\text{O}$, $\cdot\text{C}_3\text{H}_5\text{O}_2$, etc.), $n \leq 3$.

Most of the intermediate products above have been confirmed by gas chromatograph mass spectrometer (GC-MS) analysis of byproducts of NG flow experiments at FSEC. The oxidation of intermediate products (reactions 6-8), in all likelihood, occurs faster than the oxidation of NG (reaction 5).

Although the direct production of nitric acid from $\text{R}_1(\text{ONO}_2)_n$ cannot be excluded, experimental results indicate that most of the HNO_3 is produced by secondary reactions. The data obtained at FSEC indicate that NO_2 is a primary and HNO_3 a secondary product of NG photocatalytic decomposition over TiO_2 particles. HNO_3 is most probably formed via reactions involving nitrogen oxides and water (Cotton and Wilkinson 1988):



Photolytic (no TiO_2 present) decomposition of NG occurs via a different mechanism involving the scission of the weakest (O - NO_2) bond in the molecule.



Thermochemical bond energy for RO-NO₂ bond is $E_b=36.4$ kilocalorie (kcal)/mole, which is close to the reported energy of activation of NG thermal decomposition ($E_a=37.4$ kcal/mole). Hence, it appears that both photolytic and thermal decomposition of NG occur via cleavage of the RO-NO₂ bond as an initial step. After the first NO₂ splits off, the remaining unstable radical breaks down rapidly followed by the oxidation of the fragments, which yields final products.

Conclusions From Earlier Work

The initial work on UV photocatalytic oxidation was briefly described in Chapter 3. CERL, Indian Head, and ESTCP funded FSEC to perform follow-on bench-scale work involving reactors sized at 5 SCFM and 50 SCFM. Because of disappointing results during the 50 SCFM reactor testing, a new design was developed by FSEC that was designated single-cell photoreactor (SCP)-8. The research efforts associated with these reactors are described in the following sections.

5 SCFM Photocatalytic Reactor

Figure 8 shows a diagram of the 5 SCFM UV photocatalytic reactor and some of its associated instrumentation. A detailed description of the unit's design and analysis is presented in T-Raissi et al. (1995). The photoreactor was constructed of a 15.2-cm outside diameter seamless aluminum tube, 1.18-m long having a volume of 17.6 L. The reactor contained 44 perforated baffles on which TiO₂ was immobilized. The reactor also contained two 65-watt (W) low pressure mercury lamps (LPMLs) as the UV light source. The effect of many variables were studied during the course of the 5 SCFM reactor bench-scale work. A synopsis of these results follows.

Retention time.

Figure 9 shows the typical results of retention time. The results are presented in terms of space velocity, which is the inverse of retention time. Space velocity results are presented in the range of 48 to 477 hr⁻¹, which corresponds to retention times of 75 to 7.5 s. As the acetone and ethanol retention times were increased, the destruction removal efficiencies (DREs) increased. The DRE for NG was very high for all test runs. However, the NG DRE did decrease slightly at lower retention times.

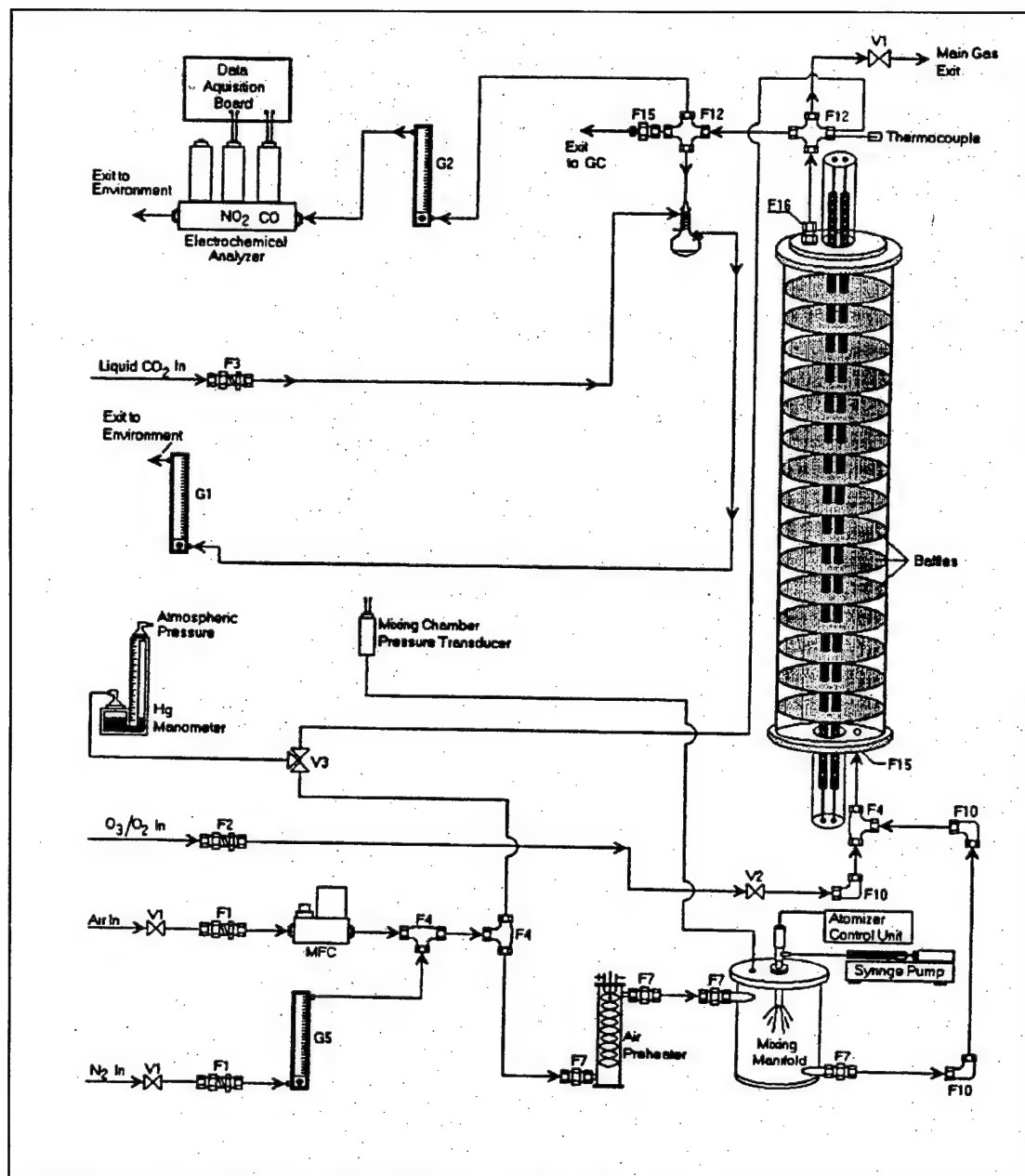


Figure 8. Schematic diagram of the 5 SCFM UV photocatalytic reactor.

NG input concentration.

A slight decrease in NG DRE occurred at the highest NG input concentrations. For example, at a retention time of 7.5 s, NG DRE dropped from 100 percent to 98.8 percent as the NG concentration input stream increased from 4.8 to 9.8 ppmv.

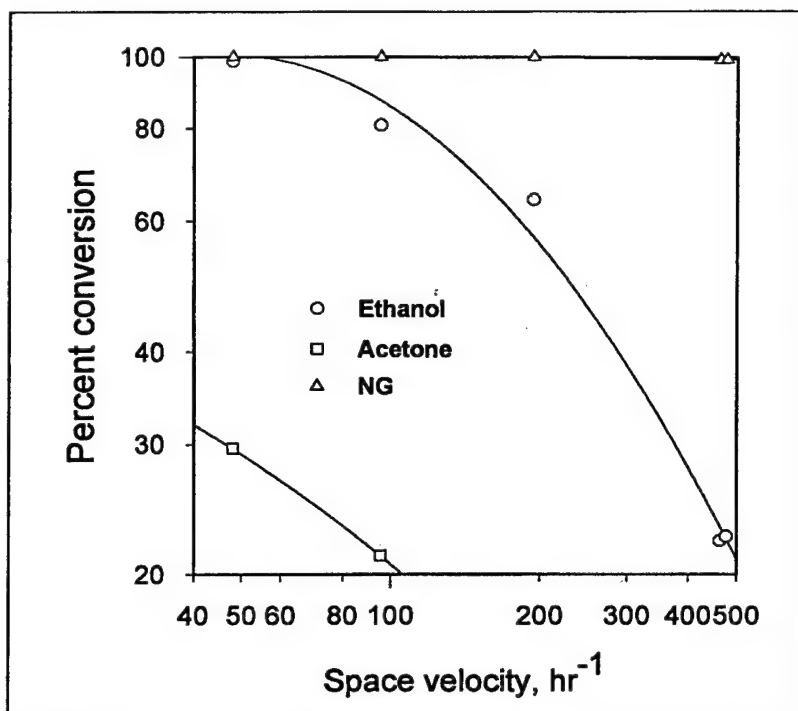


Figure 9. Effect of space velocity in 5 SCFM reactor.

Ethanol and acetone input concentrations.

Researchers studied the effects of high concentrations of acetone and ethanol that might be found at the mixing room during the dry down process. A large increase in the solvent concentration seemed to lower the DREs of all three target compounds, but the NG DRE was only lowered slightly. For example, when the input concentrations of ethanol and acetone were raised from 940 to 10,520 ppmv and 470 to 5,260 ppmv at a retention time of 7.8 s, the ethanol DRE dropped from 22.2 to 6.4 percent. Acetone removal was essentially nil at this retention time and the DRE for NG dropped slightly from 99.2 to 98.6 percent. A full-scale reactor with similar performance characteristics would selectively remove NG and allow the solvent emissions to pass through for recovery or treatment by more traditional air pollution control equipment.

Water vapor concentration.

In earlier studies with smaller reactors, water vapor was shown to markedly improve reactor performance. The water vapor seems to be a source of active radicals that aid in the oxidation of the target compounds. This trend held true for most tests on the 5 SCFM reactor. However, at high solvent concentrations and low retention times, water vapor does seem to begin inhibiting photo-oxidation. This inhibition is likely due to the water molecules occupying the active sites on the TiO_2 surface.

Added oxidants.

Tests were conducted with added oxidants to determine the effects on reactor performance. All these tests were conducted at retention times of slightly less than 8 s. FSEC studied the effects of added oxygen, ozone, and hydrogen peroxides. Oxygen had a small effect on acetone and ethanol DREs and no effect on NG DRE. Ozone had a more pronounced effect. In the photocatalytic experiments, the DREs of ethanol and acetone in the presence of ozone increased from 22.5 to 63.8 percent and from 0 to 5.3 percent, respectively. Hydrogen peroxide addition had a large effect on ethanol oxidation and no effect on acetone. In one experiment, the DRE of ethanol was doubled to 35.6 percent. The primary byproduct of the oxidation process was acetaldehyde, which is a listed hazardous air pollutant under the Clean Air Act Amendments of 1990.

50 SCFM Demonstration

The 50 SCFM photocatalytic reactor demonstration was designed to validate FSEC's reactor design and subsequently reduce the risk of scale up. The demonstration took place at two sites. The 50 SCFM unit was tested at FSEC using solvent diluted NG waste streams. FSEC fabricated a smaller single-cell reactor (SCP-7) with the exact dimensions as one cell of the 50 SCFM reactor, which was tested at Indian Head using only NG. The demonstration was never completed. During the testing, Indian Head personnel determined that the 50 SCFM reactor was not maintainable, could not achieve the desired DRE at the designed flow rate, and could not be scaled up to treat 650 SCFM using 100 lamps or less.

The poor maintainability of the system was determined after approximately 50 hr of operation. At about this time, the reagent delivery system suffered a component failure that caused contamination of the catalyst. It was decided to replace all the cartridges and rejuvenate the catalyst. This effort took well over a month and pointed out many of the potential problems that would occur in the field.

Before replacing all the catalyst cartridges, FSEC ran a series of tests using only one cell of the 50 SCFM reactor. The tests were run with the contaminated cartridges and rejuvenated cartridges. Figure 10 shows the results. This graph indicates that the reactor could nearly achieve the target DRE at the designed flow rate but, at higher flow rates, it did not come close to the requirement.

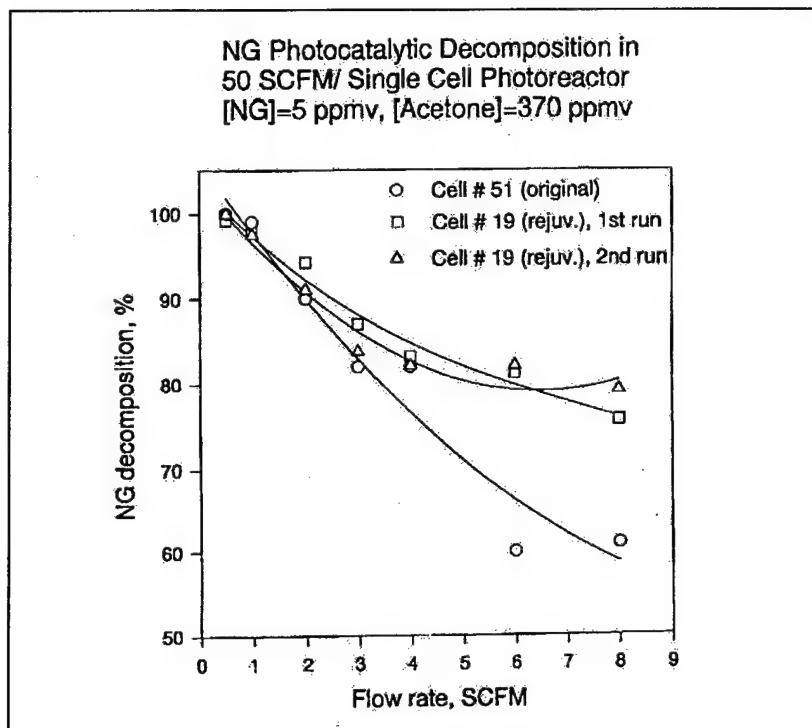


Figure 10. DRE at several flow rates for one cell of the 50 SCFM PPCU.

Prior to the tests, 100 lamps were set as the maximum number that could be used in a full-scale system. This decision was based on a theoretical calculation that Indian Head's waste stream could be treated with 75 lamps and the feeling that a 100-lamp system would push the limit of maintainability. In the system design, each lamp occupies a separate cell that functions as a reaction chamber. For a flow rate of 650 SCFM in a system with 100 cells, the flow rate through each cell would be 6.5 SCFM. The information in Figure 10 shows that the NG DRE at this flow rate for the rejuvenated cell was in the 80 percent range.

Similar tests were then run without acetone at Indian Head on the SCP-7. The contaminated air stream was generated by forcing hot air through glass wool saturated with NG and 2 percent 2-nitrodiphenylamine. Measurements of DRE were made at 2, 4, 6, and 8 SCFM and the DREs were 85, 66.5, 73, and 60 percent, respectively. Based on these results, Indian Head concluded that this design was not capable of meeting their needs.

Two alternative solutions were identified. One was to investigate a new FSEC design designated SCP-8 and the other was to investigate a larger Zentox Corporation prototype design. Indian Head tested both designs simultaneously and the results are presented in the remainder of this section.

Zentox Photocatalytic Reactor

The Zentox design was fully developed and essentially ready to test. The approach for this effort was to validate the design on a slipstream from the annealing oven and scale it up if selected. Indian Head performed two tests of the Zentox photocatalytic reactor at the annealing ovens located in Bldg. 871. The first test was performed during the week of 14 July 1997. The unit was tested at two flow rates, 25 and 75 SCFM. The results from the test indicate that the unit was effective in reducing the NG emissions to the 98 percent or greater level. Unfortunately, Indian Head did not obtain enough data to determine whether the NG was actually being destroyed or merely being adsorbed onto the catalyst and support structure. The second test of the Zentox reactor was completed 30 August 1997. Two sets of conditions were tested. The first set was of very conservative design to demonstrate successful steady-state performance. The second set was designed to provide the data required while optimizing the economics of the system. The first test was performed at 48 SCFM and resulted in a 97 percent DRE. The second test was performed at 75 SCFM with half as many filters as the first test. It resulted in a 97 percent DRE. The details of the test are presented in a final report (Turchi 1998).

FSEC SCP-8 Photoreactor

The approach for the FSEC SCP-8 testing was to verify the performance in the laboratory, generate the necessary sizing data, and, if the new design concept was selected, build a unit based on the results. Figure 11 shows the SCP-8 reactor.

The SCP-8 incorporated design improvements to aid in the adsorption of target compounds. A radial flow catalyst cartridge configuration improves adsorption by forcing the contaminated gas to pass through the catalyst bed. This type of design reduces the distance target compounds must travel to come into contact with the catalyst surface. Another critical consideration is the type of photocatalyst support used. FSEC research indicates that the best support materials are unaltered natural polymers (biopolymers) such as woven cotton cloth. These biopolymers are superior to woven inorganic glass mesh type matrices used by most researchers. The use of biopolymer support provides the best mass transfer environment by minimizing intrusions with respect to both UV light irradiance and matter transport to the photocatalyst surface. Intrusions are minimized because the titania bond much more evenly to the biopolymer surface. An explanation for this effect may be the possible hydrogen bonding between cellulose fibers and TiO_2 particles as depicted in Figure 12.

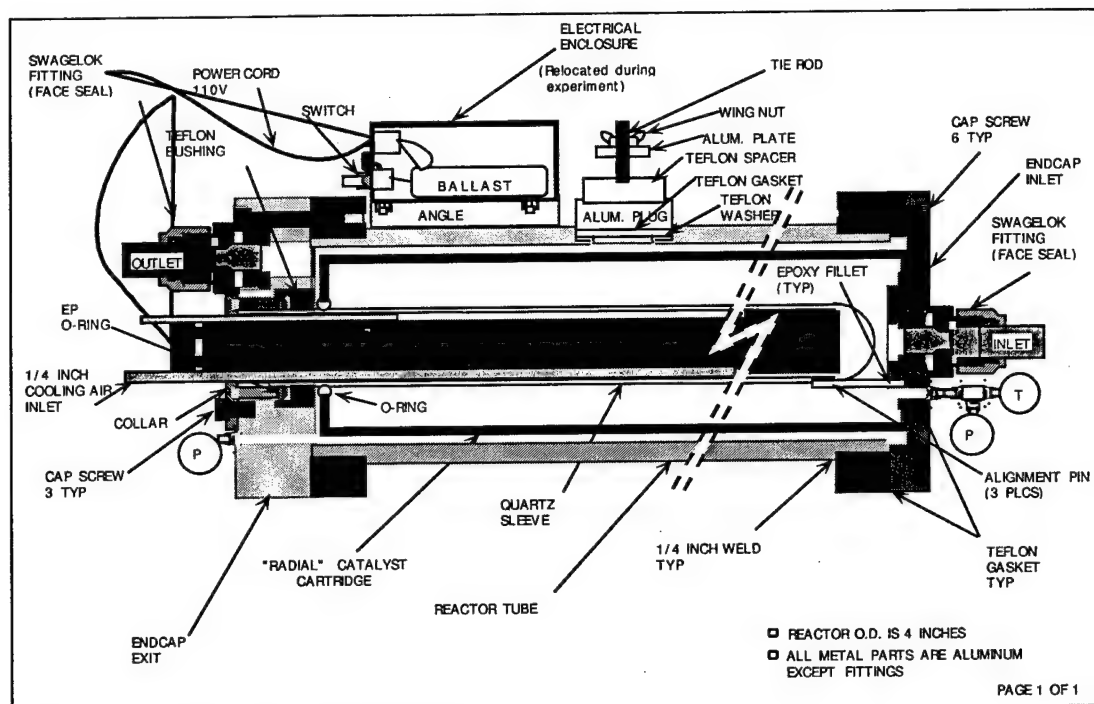


Figure 11. SCP-8 single cell photoreactor.

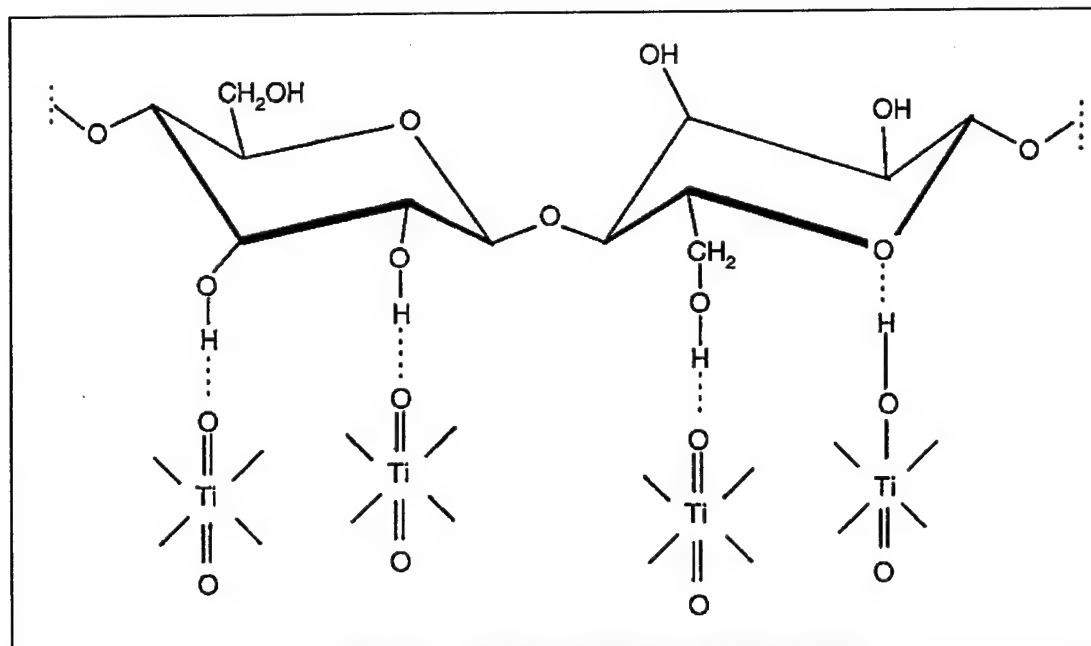


Figure 12. Possible hydrogen bonding of titania particles to cellulose fibers.

The SCP-8 was tested in the laboratory using the same setup that was used for the SCP-7 testing. Indian Head performed two small-scale tests using the SCP-8. The first test was completed in July 1997 and the second was completed in August 1997. The results from the first test were anomalous and the test was repeated. The unit was tested at 8, 10, and 12 SCFM. Several samples were taken at each flow rate, and the average DREs were 98.3, 98.6, 90.1 percent respectively. The average NG inlet concentrations were 14, 5.7, and 19.5 ppmv respectively. FSEC believes the 12 SCFM data to be on the low side because the high flow rate caused a failure at the end of the catalyst support and allowed NG breakthrough.

The results of the SCP-8 testing are presented in Figure 13. This graph shows a summary for many tests on the SCP-8 performed at both Indian Head and FSEC. The Indian Head tests introduced pure NG into the reaction chamber along with 2-nitrodiphenylamine (2-NDPA) as a stabilizer. The FSEC tests introduced NG dissolved in acetone (DMK) into the SCP-8. The graph compares NG DRE to H_{NG} , which is the inverse of the flow rate and NG concentration entering the reactor. Not surprisingly, Figure 13 shows that, as the flow rate and NG concentration increases, the NG DRE decreases. This figure also shows that near 100 percent DREs are possible with this type of reactor design.

Design Selection

The FSEC design was selected over the Zentox design for the large-scale demonstration. The FSEC design was selected because:

1. FSEC formed an alliance with Trojan Technologies, Inc., of Canada, which gave them a greater manufacturing capability than Zentox Corporation did.
2. The FSEC unit had a slightly higher performance (98 percent DRE compared to 97 percent DRE) in the tests.
3. To achieve a DRE of 99.5 percent, the FSEC design requires 6 kiloWatt (kW) of power, which is one-fifth of the energy required by the Zentox unit with similar performance.
4. Zentox provided a \$200,000 estimate for a reactor design having an 80+ percent DRE. The FSEC/Trojan unit with a DRE of 99.5 percent was estimated to cost \$225,000.

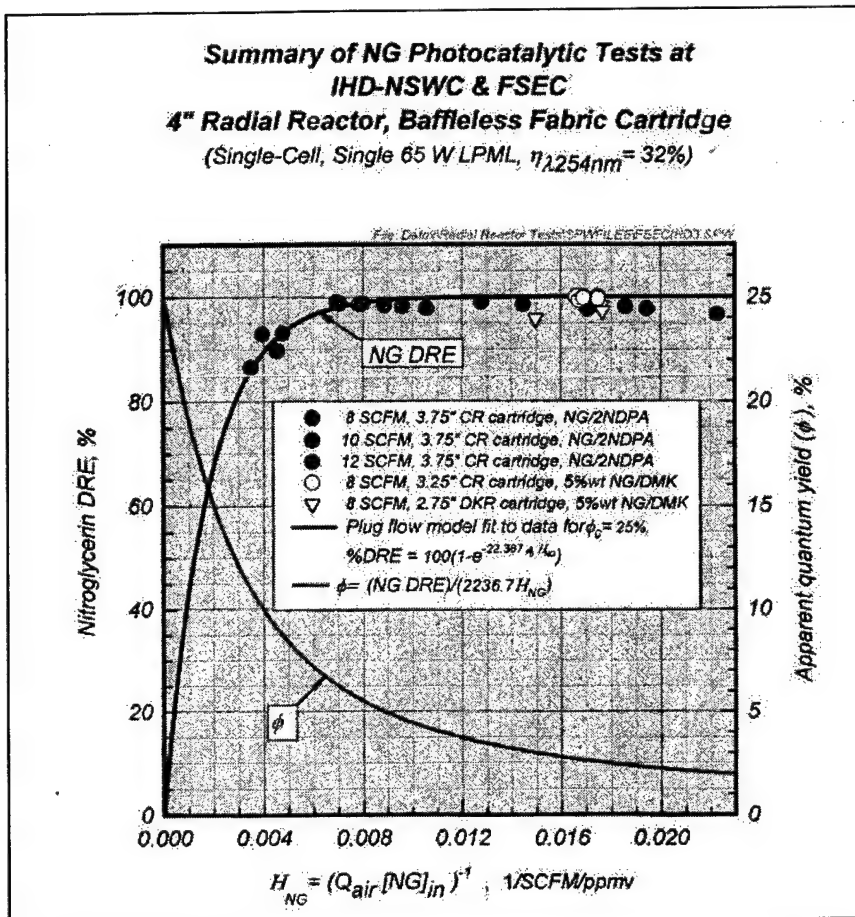


Figure 13. Summary of NG photocatalytic tests at Indian Head and FSEC.

Based on the FSEC data shown in Figure 13, FSEC designed a 650 SCFM photocatalytic pollution control unit (PPCU). Trojan Technologies, Inc. fabricated the reactor.

Description of the 650 SCFM PPCU

Design

The 650 SCFM PPCU is a pollution control device designed to treat NG and VOCs generated during the manufacture of multi-base propellants. The system uses UV light to activate TiO_2 photocatalyst-producing reactive radicals as described earlier in this section. The 650 SCFM PPCU is pictured in Figure 14.

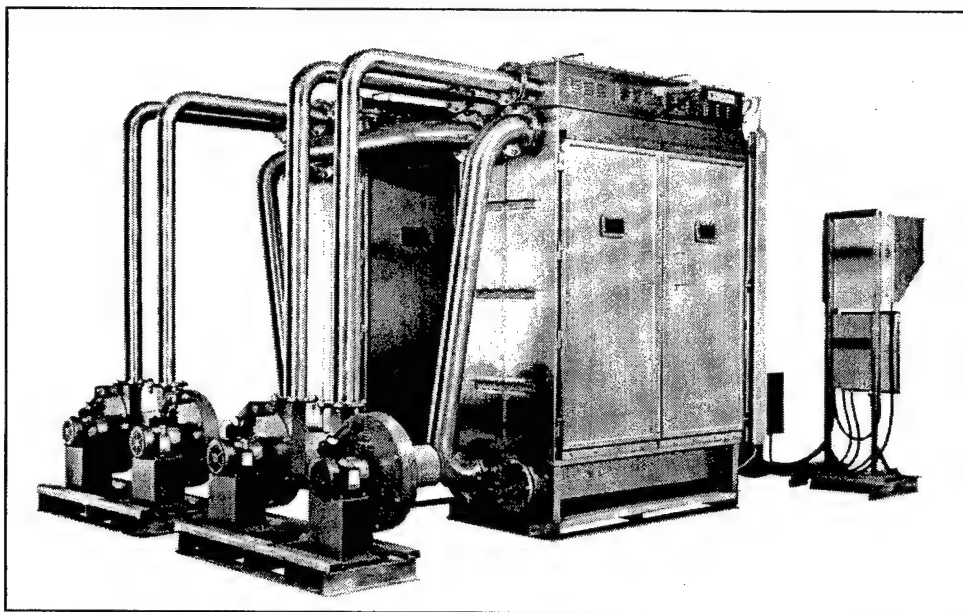


Figure 14. 650 SCFM PPCU.

Mass transfer considerations play a major role in the mineralization of organic compounds on TiO_2 support surfaces. Therefore, the reactor design must optimize the mass transfer of contaminants to the catalyst surface. The 650 SCFM PPCU uses a catalyst cartridge designed by FSEC. FSEC's catalyst cartridge uses an innovative design that optimizes gas-solid contact. Figure 15 shows details of the gas flow passage through FSEC's cartridge.

The 650 SCFM PPCU consists of two modules in parallel. The modules are positioned with the long sides parallel to each other. The modules are connected via external ductwork located on the ends of the unit. Each module is made up of two identical banks of lamps containing 16 lamps each.

The unit has a total of 64 lamps. Access to the lamps is through the top of each module via a noncontact air-cooling compartment. The lamps are separated from the contaminated fluid by an outer quartz tube. Cooling air is pumped into the quartz sleeve through a quartz dip tube and exits through vents in the side of the air-cooling compartment. Cooling air is provided by four cooling fans (one per bank) located outside of each module. The cooling air is designed to keep the temperature of the LPML around the optimum UV output temperature of 105 °F (40 °C). However, if the lamps are maintained below 130 °F (55 °C), the relative UV output will remain above 80 percent.

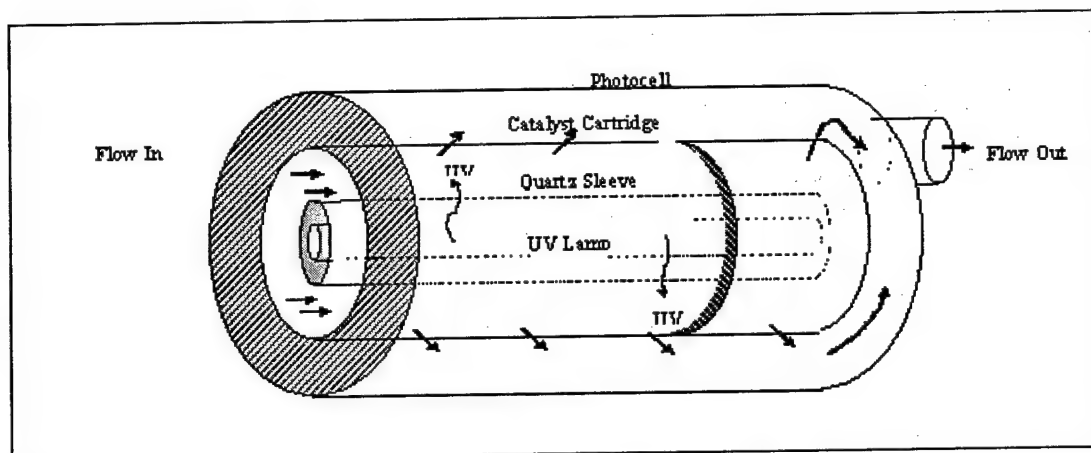


Figure 15. Details of flow passage through FSEC's catalysts cartridge.

LPMLs were selected for this application because of the lamp output and the fact that they have a relatively long life. The lamps are expected to need replacement yearly in an actual application. An LPML has a useful life of 8,500 hr. In contrast, a typical medium pressure mercury lamp has a useful life of 3 months. The outputs of both types of lamps decrease with age.

The catalyst is deposited on the inner surface of a cylindrical fabric support. The catalyst used for the 650 SCFM PPCU is Uniti 908 manufactured by Kemira, Inc. The catalyst cartridges, sometimes referred to as "socks," weigh 98 ± 2 grams (g) and have approximately 10 g of catalyst deposited on the inner surface. The catalyst loading varies by less than 5 percent along the stocking length. The typical catalyst loading for a sock is 1.9 mg/cm^2 , which is an order of magnitude greater than the loading reported in earlier work by FSEC. The increase is due to the additional surface area of the fabric compared to a flat plate.

The catalyst cartridge is placed around the outer quartz sleeve and fastened with plastic ties. The TiO_2 catalyst receives a uniform irradiance of about 3.6 mW/cm^2 in this arrangement at a 2-in. distance from the lamp axis. The catalyst cartridge attaches to an entrance port at the bottom of the bank and a bulkhead at top of the bank. Access to the catalyst cartridge is through side access doors shown in Figure 16. The socks are designed to be easily replaceable.

The 650 SCFM PPCU can be operated as a forced air or an induced flow system. The gas flow of the unit is similar to a baghouse with the gas flowing in the reverse direction. Refer to the module cross-section shown in Figure 17 as the process is described.

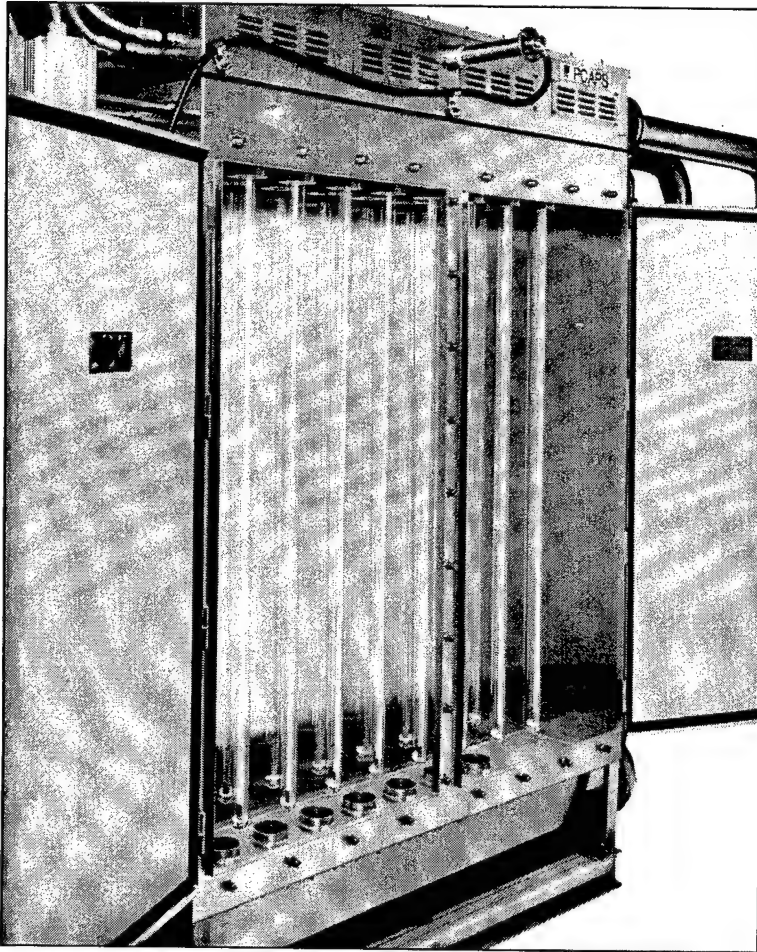


Figure 16. Interior of a 650 SCFM PPCU module.

As the contaminated flow enters the 650 SCFM PPCU, it splits so that half of it is directed to each module. Once the flow reaches a module, it enters a plenum at the bottom of the first bank or "Bank A." The contaminated gas travels into the irradiated annulus between the outer quartz tube and the catalyst support. The gas is forced through the catalyst cartridge, ensuring intimate contact between the contaminant and the activated catalyst. A large portion of the NG is removed in this first stage. The exact proportion depends on the flow rate and initial concentration of NG. The partially treated gas exits Bank A through an exit port located above the entrance port near the top of the unit. The gas is transferred to the inlet of the second bank or "Bank B" through an external conduit. The banks of each module are identical and the contaminated air flows into the bottom plenum and through Bank B in the same manner as Bank A. The second stage removes the remainder of the NG. The exhaust from each module is combined into one stack and emitted into the atmosphere.

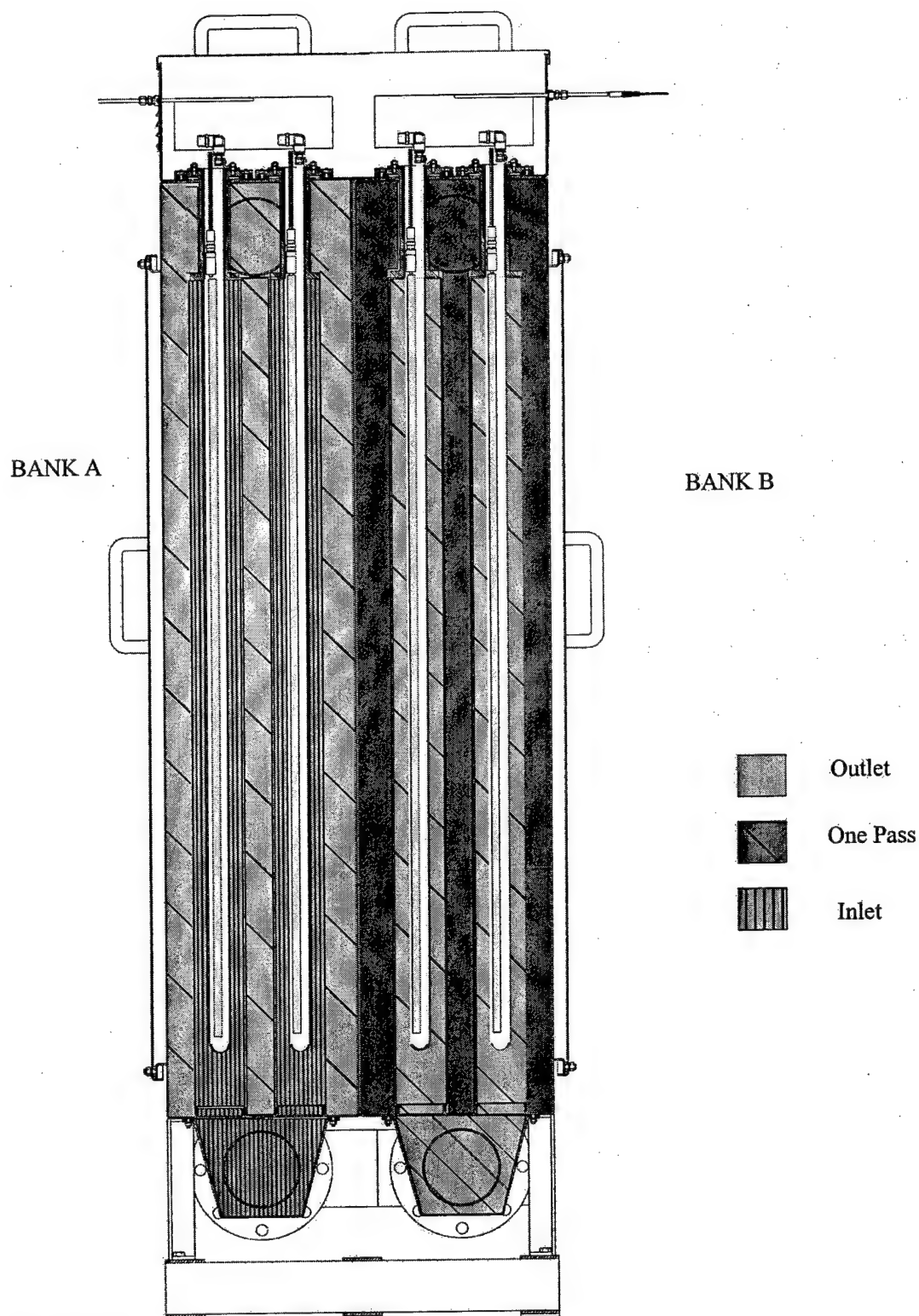


Figure 17. Cross-section of the 650 SCFM PPCU module.

The PPCU is a 5.76 kW unit powered from a single 3-phase 208-volt (V) feed. The total power consumption is 19 kilovoltamperes (kVA). The unit requires a 60-A service as it draws approximately 53 A. The low-pressure mercury lamps are standard 65-W lamps. The lamps basically emit monochromatic UV radiation with a wavelength of 254 nm. The quartz of these lamps has been modified so all of the 185 nm radiation is absorbed. These lamps do not produce ozone.

The 650 SCFM PPCU was designed to be easy to operate, control, and maintain. Once the system is set up, the only input to the system is electricity. Operating the equipment is as easy as pushing a start button. In fact, the entire PPCU can be operated remotely with one switch. This means that the PPCU can easily be included in integrated process control systems. The control system for the PPCU is the exact system used in a commercially available system manufactured by Trojan Technologies, Inc. The system is capable of monitoring the lamps and informing an operator if a lamp burns out or does not come on.

Maintenance of the PPCU is restricted to changing catalyst cartridges, changing UV lamps, and changing air filters. Assuming the unit is operating continually, the recommended maintenance schedule is to replace the air filters quarterly, and the lamps and catalyst cartridges yearly. The LPML are powered using electronic ballasts. The ballasts have an estimated life of 10 yr. The PPCU is fitted with an hour meter to record the cumulative hours of operation. This meter could be used to schedule maintenance if the PPCU was operated intermittently. All of these procedures are simple. The lamps slide into a quartz sheath that resembles a large test tube and are connected with a simple two-pin connector. The catalyst cartridges are similar to filter bags and simply slide over the outer quartz sheaths and are fastened to the unit using reusable plastic clamps. In fact, the clamps were originally intended to secure dryer vents. Replacement of the quartz sheath is easily accomplished from the top of the unit.

If an electrical problem occurs, trouble-shooting procedures have been prepared to isolate the problem area. The procedures consist of operating the unit with selected items disabled. Personnel already working at DoD installations or civilian industrial facilities can perform all the maintenance and troubleshooting procedures. If an in-house technician cannot identify the problems, a modem has been installed to allow the manufacturer to troubleshoot the system over the telephone. The only hazard that is not common is that posed by the UV radiation used. It is recommended that maintenance workers be warned of the hazards associated with UV light and that adequate warnings be posted on the unit.

Every item used to manufacture the 650 PPCU—except for the catalyst cartridges and the enclosure—are “commercial off-the-shelf” (COTS) components. In terms of materials, there is nothing special about the materials used to manufacture the catalyst cartridges and, in fact, baghouses use very similar designs. There are, however, some intellectual property issues. Many of the items used in the control system were designed and are exclusively marketed by Trojan Technologies, Inc. So duplicating the 650 SCFM PPCU for a production application would require the involvement of Trojan Technologies or a redesigned control system. A new control system could be constructed entirely of COTS parts. The catalyst cartridges are another story. FSEC has a patent for applying TiO_2 to a substrate, and they have filed a patent for the cartridge. FSEC claims the following items of the design to be proprietary.

The specific items patentable are the design of the 650-SCFM PPCU, i.e., the manner in which photocells are arranged in parallel and series combination, and the manner in which this arrangement benefits from mass transfer-free behavior of photocatalytic stockings. The cartridge design is tied to the cabinet design because of the manner in which the species transport to the fabric takes place. Therefore the design of the fabric stockings (both encased and open) and the design of the PPCU cabinet are all proprietary. For example, the tubular design of the stocking is patentable because it provides the most uniform irradiance and the particular radial flow pattern through the skin that assures intimate contact between catalyst and the waste molecules. Also, the use of only natural polymers such as the particular type of cotton fabric identified by FSEC to provide the most optimum performance is patentable. Also, the manner in which phototubes are arranged results in performance improvements approaching the maximum photoefficiency realizable. The manner in which segmentation is done, at both stockings and photocell levels, allows near-maximum photosystem performance. The specific method of immobilization of the catalyst on the fabric is critical and patentable in the context of the stockings and photocell design (Huggins 1998).

DoD completely funded the development of this technology, so the Federal Government has a worldwide, nonexclusive, nontransferable, irrevocable license to make (or have made) this invention for the government's use. If a private company wants to market this design, or certain aspects of the design, they would be required to negotiate an agreement with FSEC and possibly Trojan Technologies, Inc.

Safety

Safety personnel at Indian Head have reviewed every aspect of the 650 SCFM PPCU, and the unit has been cleared for an onsite demonstration. Some safety requirements were waived because of the limited test schedule. For example, the requirement for metal ductwork for all operations involving NG was waived and plastic ductwork was allowed.

A hazard evaluation is required before new equipment can be used at RAAP within the solvent multi-base manufacturing process. CERL funded Alliant Techsystems, Inc. (Alliant), the operating contractor for RAAP, to perform the hazard evaluation. This work was completed in 1998. Alliant has reviewed drawings of the 650 SCFM PPCU and prepared drawing review comments and process safety considerations. These results are presented in Appendix A.

Based on this initial review, the biggest safety issue to be resolved before a demonstration at RAAP can occur is the electrical rating of the UV lamp enclosure. Alliant believes the enclosures require a Class 1 Division 1 rating to prevent the waste gas stream from contacting the UV lamp. This rating applies to electrical devices in locations in which flammable gases or vapors are or may be present in the air in quantities sufficient to produce explosive or ignitable mixtures. Whether the waste gas streams at RAAP fall into this category is questionable. The lower explosion limit (LEL) for acetone is 25,000 ppmv and the LEL for ethanol is 33,000 ppmv. At the FAD operation, Figure 2 shows that the largest measured concentrations for acetone and ethanol were around 180 ppmv and 360 ppmv respectively. Unfortunately acetone and ethanol concentrations in the mixing room exhaust have never been successfully measured. The theoretical calculations of acetone and ethanol concentrations performed in Chapter 2 estimated acetone and ethanol concentrations of 513 ppmv and 804 ppmv respectively for the entire mixing cycle and 5,390 ppmv and 8,440 ppmv respectively during the dry down period. However, as discussed in Chapter 2, the dry down concentrations are probably significantly lower. If the Class 1 Division 1 rating is appropriate, a design modification of the enclosure involving the glass enclosures themselves or the cooling air may be required.

5 Demonstration

Purpose

This chapter presents information that will be useful for a demonstration of UV photocatalytic technology at RAAP. A demonstration of the 650 SCFM PPCU at RAAP's solvent multi-base lines is required to show that UV photocatalytic oxidation is a viable treatment technology for reducing NG emissions. The demonstration should focus on the two largest emission sources: the mixing room and FAD operation. If NG is removed from these waste gas streams, more traditional VOC treatment technologies could then be safely used to reduce the remaining VOC emissions. In the case of the mixing room, the solvent concentrations may be high enough for cost-effective recovery of the acetone and ethanol emissions.

A secondary objective of the demonstration should be to determine the PPCU's capability for reducing VOCs at both the mixing room and FAD operation. Since the U.S. Environmental Protection Agency (EPA) no longer classifies acetone as a VOC, the demonstration need only show significant reduction of ethanol emissions.

The demonstration of the PPCU at RAAP will occur after the demonstration of the same PPCU at Indian Head. As explained in Chapter 1, MSE Technology Application, Inc. will be responsible for this demonstration. CERL will provide oversight of demonstration activities. The specific components of the PPCU demonstration plan at RAAP will depend heavily on the results of the Indian Head demonstration. The demonstration at RAAP will attempt to build upon and confirm the Indian Head results.

Three industries could benefit from UV photocatalytic technology: manufacture of NG-containing pharmaceuticals, manufacture of extruded rocket motors, and manufacture of solvent multi-base propellant. Collectively these three industries do not represent a large market for this technology. The real payoff for the development of photocatalytic oxidation is in its ability to treat VOCs. Although each application needs to be thoroughly investigated, the demonstration of the

650 SCFM PPCU at RAAP and Indian Head will provide an impetus for further development in this area.

Equipment Setup for Demonstration

The 650 SCFM PPCU equipment setup is pictured in Figure 18. The photograph shows the PPCU located behind an annealing oven facility at Indian Head. The unit is resting on a temporary 12 ft x 16 ft plywood deck. The 650 SCFM PPCU will be connected to treat a slipstream of the waste gas from the mixing room and FAD operation. A 650 SCFM slipstream is about 30 percent of the flow from the mixing room and 13 percent of the flow from a FAD building. The flow rate of the slipstream will be controllable. The ductwork and the PPCU must be insulated to inhibit condensation. The bottom chamber and the sides of the PPCU are already insulated with 1-in.-thick foil-faced rigid fiberglass insulation. Additional ductwork must also be insulated in a similar fashion.

An auxiliary fan will be used to provide the required flow rate through the 650 SCFM PPCU. The fan will be attached to the PPCU exit port so that gas is pulled through the unit. The auxiliary fan is not integrated into the control system of the PPCU but will be operated independently. The flow will be controlled manually using a butterfly valve attached to the fan exit. The fan will be located near the power distribution center (PDC).

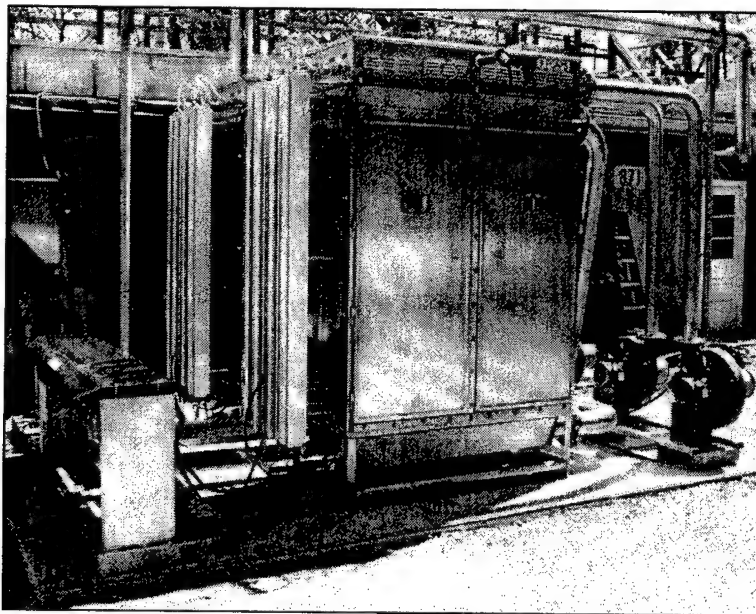


Figure 18. 650 SCFM PPCU equipment setup.

A filter will be placed upstream of the PPCU to minimize dust and pollen entering the unit. Dust contamination can adversely affect the unit's performance. Dust could (1) coat the quartz sleeve and block the light, (2) coat the catalyst and prevent the target contaminant from contacting the catalyst, or (3) coat the catalyst cartridge and affect the flow through the cartridge.

Sample ports for NG and VOC measurements will be located in the vertical sections of ductwork connected at the inlet and outlet. To help provide an evenly distributed flow, the ports should be positioned so that there are 4 ft of straight ductwork on the upstream side and at least 2 ft of straight ductwork on the downstream side.

The NG sampling probes will be sized so that the sampling is as close to isokinetic as possible. Isokinetic sampling requires that the sample be drawn into the probe at the same velocity as the exhaust stream is flowing through the ductwork. The goal of isokinetic sampling is to obtain a representative sample of particulate matter in gas streams. Particulate matter should not be present in the waste gas stream. However, there is a slight chance that some NG may condense into an aerosol, and isokinetic sampling would allow a representative sample of the NG aerosol.

To control the PPCU, the operator interfaces with the System Control Center (SCC) via local or remote terminals. All communications to and from the PDC originate from the SCC via an RS422 serial link. The PDC also houses the communication board, which controls and monitors the UV lamps, the thermal management system, and the switches that operate the cooling fans. The PPCU can be run in one of two modes—automatic or manual. A combination of these settings will probably be used during the testing. All 64 lamps and the thermal management system can be turned on/off remotely in automatic mode. The modules cannot be controlled independently in automatic mode. In manual mode the modules can be operated independently allowing operation of half the system. Each bank can be operated independently and each set of eight lamps can be turned on and off within a bank.

Parameters To Study

To achieve the objectives of the PPCU demonstration, the following parameters must be measured:

- Temperature upstream and downstream of PPCU, ambient temperature, and temperature within the quartz sleeves
- Ambient humidity
- Flow rate through the PPCU
- Pressure drop across the PPCU and pressure difference between the cooling air in the quartz sleeves and the waste gas stream in the PPCU
- NG concentrations upstream and downstream of the PPCU
- NG concentration on catalyst
- NO_x concentrations in the ambient air and downstream of the PPCU
- Acetone and ethanol concentrations upstream and downstream of the PPCU.

Temperature and humidity.

Thermocouples will be used to monitor the temperatures in the system. One thermocouple will be inserted into the ductwork near the PPCU inlet and one thermocouple will be inserted into the ductwork near the outlet of the unit. The cooling gas temperature is controlled by the PPCU. Thermocouples are located in the cooling air chambers and the temperatures are displayed on the controllers. The ambient temperature and humidity will be monitored with a battery-operated psychrometer.

Flow rate.

To quantify the flow rate, a standard pitot tube and EPA method 2C will be used. The pitot tube will be inserted into the ductwork upstream of the PPCU. The pitot tube will be positioned so that there are 4 ft of straight ductwork on the upstream side and at least 2 ft of straight duct work on the downstream side. The pitot tube will be connected to a manometer to record the velocity pressure.

Pressure.

The differential pressure through the PPCU will be measured periodically using an inclined manometer connected to pressure taps built into the ductwork just upstream and downstream of the PPCU. Additionally, the absolute pressure will be measured in the quartz sleeves. This quartz sleeve pressure will be compared with the PPCU inlet pressure to show that a relative positive pressure is always maintained. This positive pressure will prevent contact between the waste gas stream and the UV lamp if a crack develops in the quartz sleeve.

NG concentrations.

NG concentrations will likely be measured by a continuous emission monitor (CEM) developed by Environvisions, Inc. This NG CEM was developed as part of Indian Head's ESTCP project. The CEM was developed to reduce the cost of validating the PPCU by providing near real time analysis of NG concentrations. The NG CEM will be evaluated during the Indian Head demonstration. If the monitor is shown to be accurate, it will be used as the main NG measurement device during the demonstration at RAAP.

The NG monitoring method is depicted in Figure 19. Samples containing low levels of NG are passed through reagents that react with the NG and change color. The color difference is measured by a spectrophotometer and used to provide a quantitative measure of the sampled NG. The design cycle time for the instrument is 30 min. Half of the cycle is used for sample collection. The instrument consists of three modules.

The first module is the NG sample capture module. It consists of an air sampling pump, a polymeric sorbent column, electronically controlled valves, and an integral thermal desorption oven. The module draws an air sample through a sorbent column over a 15-min period. The sample is then thermally desorbed for introduction to the next module and the column is purged and reconditioned for the next sampling cycle.

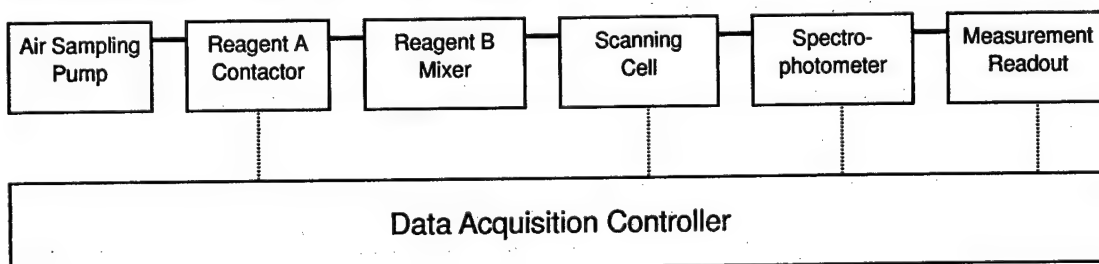


Figure 19. Block diagram for NG continuous emission monitor.

The second module is the mixing/reaction module. It contains a catalytic reaction chamber into which reagents are metered with an electronically controlled pump. In this module the concentrated NG vapor is mixed with liquid reagents and allowed to react and change color in the presence of a zinc catalyst. The mixture is then introduced to the third module. The sample lines and chamber are then purged and reconditioned for the next sampling cycle.

The final module is the colorimetric measurement/data acquisition module. This module consists of a 1-m long cell and a spectrophotometer. The liquid reactant is introduced to the cell using an electronically controlled peristaltic pump, and the intensity of the liquid's color is measured with a fiber optic link to the spectrophotometer. The color intensity is then interpreted as NG concentration by the computer controller.

Several sorbent tube samples will also be collected to verify the performance of the CEM. A modified version of Occupational Safety and Health Administration Method 43 will most likely be used to validate the NG CEM results.

NG on the catalyst.

The concentration of NG remaining on the catalyst cartridges will be measured using a procedure that will be developed by Indian Head during their demonstration. The procedure will involve extracting the NG out of the catalyst cartridge, filtering the extract (because it will probably contain TiO_2), and analyzing the extract with high pressure liquid chromatography.

NO_x concentrations.

A chemiluminescent NO_x analyzer conforming to EPA Reference Method RFNA-1194-099 will be used to measure NO_x concentrations in the PPCU exhaust and ambient air. Dilution of the gas stream with zero air may be required to generate a NO_x concentration within the operating range of the analyzer.

Acetone and ethanol concentrations.

A photoacoustic infrared multi-gas monitor or another comparable real time monitor capable of measuring both acetone and ethanol concentrations will be used to measure acetone and ethanol concentrations upstream and downstream of the PPCU. The monitor results will be checked against a standard EPA stack gas tests such as EPA Method 18 to assure data quality.

Test Plan

There are several performance questions to answer during the demonstration of the 650 SCFM PPCU:

1. Can the PPCU remove NG from the waste gas streams and, if so, under what conditions?
2. Can the PPCU remove ethanol from the waste gas streams and, if so, under what conditions?
3. How long must the PPCU be operated to remove NG adsorbed onto the catalysts after the PPCU is no longer treating a waste gas stream?
4. Will catalyst cartridge performance degrade over time and, if so, is the performance drop due to fouling?
5. What are the effects of ambient humidity on the performance of the PPCU?
6. Can a relative positive pressure be maintained in the quartz sleeve during all test conditions?

To answer the first two questions, the DRE of the PPCU for NG and ethanol must be determined. The DRE is determined by measuring NG and ethanol concentrations at the inlet and the outlet of the PPCU and applying the following equation:

$$\text{DRE} = 1 - [\text{Outlet Concentration}] / [\text{Inlet Concentration}]$$

A 99 percent or greater DRE for NG and an 85 percent or greater DRE for ethanol will be considered as acceptable. Acetone DRE will also be measured, but the performance of the PPCU will not be judged by acetone DRE since acetone is no longer considered a VOC by regulators.

One of the basic goals of the demonstration will be to first determine the minimum conditions where 99 percent DRE for NG is achieved and then determine the minimum conditions where 85 percent DRE for ethanol NG is achieved. This information can then be used to predict the configuration and operating parameters of a full-scale PPCU.

Only two parameters will likely be varied during the demonstration: the configuration of the PPCU and the slipstream flow rate. The PPCU is currently designed so that the waste gas stream passes through two catalyst cartridges in series within a single module as shown in Figure 17. However, the two available modules can also be connected in series so that the waste gas stream passes through four catalyst cartridges in series. The additional two catalyst cartridges would significantly add to the capacity of the PPCU, but the added flow path would increase the pressure drop across the PPCU. Increasing the pressure drop across the PPCU increases the fan requirement for the system. The slipstream flow rate will be controllable through a butterfly valve. Decreasing the flow rate will increase the retention time in the PPCU allowing for more complete mineralization of the air contaminants. The tradeoff in this case is that lower slipstream flow rates translate into larger PPCU volume and catalyst cartridge requirements.

The initial PPCU configuration and slipstream flow rate will be determined by studying the results of the Indian Head demonstration and perhaps the results of single catalysts cartridge tests. At RAAP the 650 SCFM PPCU will first be demonstrated at the FAD operation. The initial setpoint for PPCU configuration and flow rate will be designed to remove just NG from the gas stream. Each of the subsequent test conditions will be based on results of previous tests and the goal of answering performance questions 1 and 2.

The intensity and type of light source, the catalytic surface area, and configuration of the catalyst used were investigated thoroughly during the earlier phases of this program (see Chapter 4). Much effort has been expended to optimize these components for the 650 SCFM PPCU, and they will not be varied during the testing. The catalyst used in the reactor is Kemira, Inc. Uniti® 908 dried titanium hydrolysate.

How long must the PPCU be operated to remove NG adsorbed onto the catalysts after the PPCU is no longer treating a waste gas stream? The answer to this performance question is important since any buildup of NG in the PPCU is a potential safety hazard. The NO_x concentrations at the PPCU outlet will be used to answer this question. Since NO_x is generated from NG oxidation in the PPCU, an outlet concentration of NO_x at or near the background ambient level is an indication of complete mineralization of all NG remaining in the PPCU. The time it takes the PPCU to achieve complete mineralization of NG could be an important factor in the overall economics of this technology. NG analyses will be

performed on catalytic cartridge samples to further assure that all NG has been destroyed during the tests.

Will catalyst cartridge performance degrade over time and, if so, is the performance drop due to fouling? If the PPCU performance begins to drop during the demonstration, a likely explanation is that the catalyst cartridges are beginning to fail. The durability of the catalyst cartridges is important in the economics and overall desirability of the UV photocatalytic technology. The most likely reason for catalyst performance drop is the fouling of the catalysts' surface by contaminants in the gas stream. Another possible reason is the loss of catalyst material attached to the fabric in the cartridge. Useful cartridge life will be measured primarily by the performance of the PPCU during the demonstration. If the DRE for NG or ethanol begins to noticeably decrease, the catalyst cartridges will be replaced to see if the DREs return to expected levels. The cartridges will also be inspected after each test for catalyst fouling and detachment of the catalysts from the cartridge fabric. Any presence of catalyst in the outlet sampling streams will also be noted. It is hoped that a single charge of cartridges can be used during the entire demonstration. Before the RAAP demonstration begins, researchers will decide whether to use the catalyst cartridges from the Indian Head demonstration or to replace them with new cartridges.

What are the effects of ambient humidity on the performance of the PPCU? The answer to the fifth performance question is important since previous studies by FSEC (T-Raissi 1997) have shown that water vapor content is a factor in the performance of a UV photocatalytic reactor. The presence of water vapor in the air has a double effect. On one hand, it increases photocatalytic activity by increasing the concentration of the active radicals on the catalyst surface. On the other hand, it ties up active sites on the catalyst surface, thus potentially reducing DREs of the target compounds. In general, FSEC has found that the presence of water vapor increases the DRE for NG. It is suspected, however, that high water vapor concentrations cease to be beneficial and perhaps become detrimental. During the demonstration, all the water vapor found in the waste gas streams will come from the ambient air. The ambient air humidity will be measured for all tests. However, it will be difficult to develop a correlation between water vapor concentration and PPCU performance because the humidity will not be controlled and the test conditions will be changing at the same time the humidity levels are changing. The demonstration should determine if normal ambient humidity is sufficient to maintain the PPCU's performance.

Can a relative positive pressure be maintained in the quartz sleeve during all test conditions? This performance question relates to the safety of the PPCU in the event a crack forms in the quartz sleeve. If the pressure in the quartz sleeve remains positive relative to the gas stream passing through the PPCU, then air will flow out of cracks into the waste gas stream. In this way, direct contact between the waste gas stream and the UV lamp is prevented. The cooling air fans will produce the positive pressure in the quartz sleeve and the fan for the PPCU will pull air through the PPCU. At the FAD operation, a fan pushes air through the FAD room. At the mixing room, a fan pulls air through the mixing room, but this fan will be upstream of the PPCU. Because of these complex fan interactions, it is difficult to predict the pressure that will occur in the PPCU during the demonstration. The pressure measurement occurring during all tests will indicate whether a quartz sleeve crack would be a serious problem in a similar full-scale configuration. The pressure measurements can also be used to predict full-scale PPCU fan and cooling air fan requirements for this configuration. If this type of retrofitted configuration does not seem feasible, it would be possible to replace the existing FAD operation and mixing room fans with a single fan to pull waste gas both through these operations and through the PPCU. As a further precaution, a full-scale PPCU could be designed to vent the waste gas stream to the atmosphere in the event of cooling air pressure loss.

Some nonperformance-related PPCU criteria such as versatility, reliability, maintenance requirements, and ease of use will be examined during the course of the demonstration. Since the waste gas streams at RAAP are significantly different than at Indian Head, the RAAP demonstration will be a good test of the PPCU's ability to handle alternate air pollution streams containing organic compounds. The reliability of the PPCU will be measured by the ability of the unit to provide trouble free performance during the demonstration. Except for the catalyst cartridges, the components of the PPCU have been proven in the commercial sector and a mechanical failure of the PPCU during the limited time frame of the demonstration is unlikely. The limited timeframe will also restrict an examination of the PPCU's maintenance requirements. No maintenance will be scheduled during the demonstration. Chapter 4 describes 650 SCFM PPCU maintenance. The system's ease of use will be measured primarily by noting any difficulty in operating or maintaining the system.

Several engineers and technicians will be involved during the course of the demonstration to facilitate data collection and safe system operation. During all tests, the regulation of the PPCU operating temperature and the integrity of the quartz sleeves will be monitored. Any problem of this type will cause testing to

be abandoned until corrections are achieved. In normal operation the unit would probably be controlled through a PLC and would require only occasional inspections by the operator.

When the demonstration is complete, the PPCU will be decontaminated using standard RAAP procedures. The spent NG killer and water solution will need to be disposed of as hazardous waste by RAAP.

Demonstration Schedule

The demonstration schedule depends primarily on the solvent multi-base propellant manufacturing schedule at RAAP. RAAP is not currently manufacturing solvent multi-base propellant but may begin manufacturing large quantities of the propellant M30A1E1 around the year 2000. RAAP expects to perform a test of this propellant manufacturing process in March 1999. The test will be fairly significant in its scope and will last 1 to 2 months. This test should allow enough time to complete the necessary demonstration activities.

If a large delay in the propellant manufacturing test schedule occurs, a backup plan using the facilities at Indian Head will be used. While this demonstration would not be as ideal as a test at RAAP, Indian Head is capable of generating emission streams that are very similar to the emissions at RAAP.

6 Conclusions

The overall objective of this research is the abatement of VOCs from solvent multi-base propellant production. This report described the efforts taken to characterize the sources of the pollution, to bench test technologies most likely to mitigate the pollutants, to select the best technology for further testing, and to develop testing parameters and design for further tests at RAAP.

Characterization of Emission Sources

Existing emission studies were analyzed and additional studies performed to characterize the air emissions sources for the solvent multi-base propellant manufacturing process. Studies performed by Hercules Inc. and by Roy F. Weston, Inc. provided information about emission streams from this source. The Hercules study concluded that approximately 65 percent of the VOC loss occurred during the mixing stage and 20 percent occurred at the FAD operation, for a total of about 85 percent of all VOC emissions from the manufacturing process. The emissions represented approximately 0.3 lb of solvent loss per pound of propellant produced.

The Weston study reported an average flow rate of 2,146 SCFM through the mixing rooms. This information combined with the mass loss information presented in the Hercules report allowed the calculation of theoretical acetone and ethanol concentrations from the mixing room. The mass balance study reported about a 39.46 lb/mix loss of acetone and a 48.97 lb/mix loss of ethanol. The study also reported that about 75 percent of the emissions occurred during the dry down period. The dry down would then account for 29.6 lb/mix loss of acetone and 36.7 lb/mix loss of ethanol. If a 3.5-hr mixing cycle is assumed, the emission rate is 11.27 lb/hr for acetone and 13.99 lb/hr for ethanol. The calculated concentrations are 513 ppmv for acetone and 804 ppmv for ethanol over the entire mixing cycle.

Bench Tests of Likely Technologies

All types of adsorption, thermal oxidation, biofiltration, and condensation technologies were considered and eliminated for economic or safety reasons. The three technologies selected for study were sulfuric acid scrubbing, bioscrubbing, and UV photocatalytic oxidation. These technologies were selected based on their potential for safe control of the multi-base waste gas streams at RAAP.

After testing of the three technologies by NJIT, Clemson, and FSEC, UV photocatalytic oxidation was selected for further development. It was concluded that this pollution control technology had more advantages than the other technologies tested. Safe operation is achievable, operation with long down times is possible, production of other waste streams does not occur, and the method potentially can remove NG from waste gas streams selectively.

Development of Equipment and Testing Parameters

FSEC designed the SCP-8 photocatalytic reactor, which was successfully tested on a small scale at Indian Head. Based on the results of the small-scale testing, FSEC designed a 650 SCFM PPCU to be used for large-scale testing at Indian Head and, based on the results of the demonstration, at RAAP. Testing will focus on the two largest emissions sources: the mixing room and the FAD operation.

The final purpose of this study was to develop information for testing of UV photocatalytic oxidation. Measurements will be taken for temperature, flow rate, humidity, differential pressure, NG concentrations up- and downstream of the PPCU, NG concentrations on the catalyst, NO_x concentrations in the ambient air, and acetone/ethanol concentrations up- and downstream of the PPCU. Some nonperformance-related PPCU criteria such as versatility, reliability, maintenance requirements, and ease of use will also be examined during the course of the demonstration.

The UV photocatalytic reactor demonstration schedule will be based on the solvent multi-base propellant manufacturing schedule at RAAP. If the schedule is significantly delayed, the facilities at Indian Head may be used. Results of the testing will be documented in a future technical report.

References

- Cotton and Wilkinson, *Advanced Inorganic Chemistry*, Interscience Pub., NY, 1988.
- Dames and Moore, Inc., "A Cost Comparison of VOC Recovery and Collection Technologies for Use in Propellant Manufacturing Operations at Radford Army Ammunition Plant, Radford, Virginia," February 1995.
- Glaze, W.H., "An Overview of Advanced Oxidation Processes for Water and Wastewater Treatment," *Book of Abstracts*, 1st International Conference Advanced Oxidation Technologies for Water and Air Remediation, Al-Ekabi, H., Ed., Science & Technology Integration, Inc., London, ON, Canada, 1994.
- Hammervold, R.E., "Development of an Innovative Sorptive Slurry Bioscrubber," Masters thesis, Clemson University, Dept. of Environmental Systems Engineering, December 1995.
- Huggins, M.C., of FSEC, email to Mike Lateulere of Indian Head, 21 April 1998.
- Hume, J.M., and W.J. Worrell, "PE-900, Volatile Organic Compound Survey of Multi-Base Production," Hercules Incorporated, January 1993.
- Langford, T.H., J.S. Todd, and D.D. Price. *Modernized FAD For Multibase Propellants*, U.S. Army Armament Research and Development Command, Large Caliber Weapon Systems Laboratory, January 1983.
- Liu, Y., D. Hanesian, and E.C. Roche. "Removal of Volatile Organic Compounds (VOCs) Acetone and Ethyl Alcohol Emitted in the Manufacture of a Multi-Base Propellant," New Jersey Institute of Technology, August 1992.
- Muradov, N.Z., A. T-Raissi, C.R. Painter, M. Lateulere, and M.R. Kemme. "DR-FTIR Characterization of the TiO₂/Support for Gas-Phase Photocatalytic Destruction of NG," 3rd International Conference on TiO₂ Photocatalytic Purification and Treatment of Water and Air, September 1997, Orlando, FL (Science & Technology Integration, Inc., Univ. of Western Ontario).

- Ottengraf, S.P.P., and R. Diks. "Biological Purification of Waste Gasses," *Chimicaoggi*, 41-45, May 1990.
- Overcamp, T.J., H.C. Chang, and C.P.L. Grady, Jr. "An Integrated Theory for Suspended-Growth Bioscrubber," *Journal of the Air & Waste Management Association*, 43(5): 753-759, 1993.
- Overcamp, T.J., B.F. Smets, R.E. Hammervold, and C.P.L. Grady, "Development of an Innovative Bioscrubber for Volatile Compounds: Phase I," Clemson University, April 1994.
- Overcamp, T.J., B.F. Smets, R.E. Hammervold, and C.P.L. Grady, "Development of an Innovative Bioscrubber for Volatile Compounds: Phase II --- Construction," Clemson University, September 1995.
- Overcamp, T.J., B.F. Smets, C.P.L. Grady, and R.E. Hammervold, "Innovative Bioscrubber Technology Development --- Phase I," Clemson University, February 1996.
- Roy F. Weston, Inc., "Air Emission Sampling Report, Multi-Base Propellant Mixing Operation, Radford Army Ammunition Plant, Radford, Virginia," May 1998.
- T-Raissi, A., and N.Z. Muradov. "Radiant Detoxification of Airborne VOCs," Florida Solar Energy Center, Contract No. N00174-91-C-0161; FSEC-CR-514-92, July 1992.
- T-Raissi, A., N.Z. Muradov, E. Martin, C.R. Painter, M. Lateulere, and M.R. Kemme. "Surface Irradiance Considerations in the Design of Vapor Phase Photocatalytic Reactors," 3rd International Conference on TiO_2 Photocatalytic Purification and Treatment of Water and Air, September 1997, Orlando, FL (Science & Technology Integration, Inc., Univ. of Western Ontario).
- T-Raissi, A., N.Z. Muradov, D. Muzzey, S. Jaganathan, E. Martin, and D.L. Block. "Photocatalytic Detoxification of Airborne VOC's (Phase II Final Report)," April 1997.
- T-Raissi, A., N.Z. Muradov, D. Muzzey, S. Jaganathan, E. Martin, C.R. Painter, and M.R. Kemme. "Designing and Costing a 50 SCFM Photocatalytic Unit for Selective Oxidation of NG and Solvent Vapors in Air," Joint Army-Navy-NASA-Air Force (JANNAF) Safety and Environmental Protection Subcommittee Meeting, 5 December 1995.

Turchi, C., and R. Miller, "Photocatalytic Oxidation of Energetic Compounds from a Propellant Annealing Oven, 8th International Symposium on Chemical Oxidation, Technology of the Nineties, April 1998.

Urbanski, *Chemistry and Technology of Explosives*, Pergamon Press, Oxford, 1965.

Appendix A: Risk Assessment of 650 SCFM Photocatalytic Pollution Control Unit

Memorandum

Radford Army Ammunition Plant
P.O. Box 1
Radford, VA 24141-0100

Date: August 28, 1998

Subject: Risk Analysis of the PPCU

To: D. A. Musser
Plant Process Engineer

From: R. E. Dodson
J. M. Gabbert
Organization: Hazards Analysis
MS: Bldg. 220
Telephone: 7551

c: K. D. Dolph
M. L. Griffith
Jeff Kelly
D. S. Hall
Hazards file (2)

HI-98-M-020

Risk Analysis of a 650 SCFM Photocatalytic Pollution Control Unit

Objective

The objective of this final report is to perform and document a Risk Analysis (RA) for a 650 SCFM Photocatalytic Pollution Control Unit (PPCU). The PPCU was designed to reduce NG vapors from entering the atmosphere from forced air dry and mixer operations. The purpose of the RA is to quantitatively determine the probability of occurrence for critical hazards identified in the Failure Modes and Effects Analysis (FMEA) presented in the Preliminary Hazards Analysis report. This report satisfies the requirements of Tasks 4 and 5 as defined in the project scope of work.

Summary and Conclusions

A quantitative Risk Analysis (RA) determined that the overall probability of a hazardous event occurring during normal or abnormal operation of the PPCU is an unacceptable $1.0E-3/h$. The RA is based on the FMEA reported previously, review of drawings for the PPCU submitted by Trojan Technologies Inc., on-site review of the unit at the Naval Surface Warfare Center (NSWC), Indian Head Division, Maryland, and discussions with NSWC Indian Head personnel. The potential hazard with the highest probability of occurrence is the initiation of solvent vapors in the process from the use of non-rated

electrical equipment (air flow assist fan). Elimination of this potential hazard reduces the overall risk to an acceptably safe $2.5E-7/h$ of PPCU operation. No catastrophic failures were identified. The RA of potentially critical safety hazards identified in the PHA is presented in Table 1.

Future Work

No additional work is planned at this time. The PPCU must be hazards assessed to the requirements of OSHA 1910.119(e) before the unit may be installed and operated at the Radford Army Ammunition Plant (RFAAP).

Recommendations

Recommendations to mitigate or eliminate potential hazards are contained in the FMEA which is included in Appendix B.

Introduction

The manufacture of solvent based multi-base propellants at RFAAP emits large quantities of both alcohol and acetone and smaller amounts of nitroglycerin to the atmosphere. In FY93 CERL began a research project to develop safe control technology for the multi-base propellant lines. One promising technology is ultraviolet (UV) photocatalytic destruction. The research effort has been a joint project between the Army and Navy. A product of this effort has been the development of a 650 SCFM prototype photocatalytic air purification device. The first unit of this design was fabricated by Trojan Technology Inc. and installed for testing at the Naval Surface Warfare Center, Indian Head Division, Maryland. A hazards evaluation of the unit was requested to be done by Radford Hazards Analysis to compliment the safety effort in progress by Indian Head personnel. The purification unit is scheduled for testing at Indian Head in July 1998. Plans are to move the unit to Radford for testing with local forced air dry and solvent propellant mixing operations after testing is complete at Indian Head.

Process Description

The 650 SCFM photocatalytic pollution control unit (PPCU) is a pollution control device designed to treat nitroglycerin (NG) vapors generated during the manufacture of double and triple base solvent propellant. The system uses ultraviolet light to activate titanium dioxide photocatalyst, producing reactive radicals. These reactive species attack airborne NG, resulting in complete reduction of the molecule to NO_2 , CO_2 , and H_2O . The PPCU is shown in Figure 1.

The PPCU consists of two identical modules. The modules are positioned with the long side parallel to each other. The modules are connected together via external duct work located on the ends of the unit. Each module is made up of two identical banks of lamps and each bank contains 16 lamps. The total number of lamps is 64. Access to the lamps

is provided via the top of each module through a non-contact cooling air compartment. The lamps are separated from the contaminated air by an outer quartz tube. Cooling air is pumped into the quartz sleeve via a quartz dip tube and exits through the vents located in the side of the cooling compartment. Cooling air is provided by four cooling fans (one per bank) that are externally located to each module. The catalyst is deposited on the inner surface of a cylindrical fabric support. The titanium dioxide catalyst support or "catalyst cartridge," is placed around the outer quartz sleeve. The titanium dioxide catalyst receives a uniform irradiance in this arrangement. The catalyst cartridge attaches to an entrance port at the bottom of the bank and a bulk head at the top of the bank. Access to the catalyst cartridges is provided by removable side access doors. The catalyst cartridge is designed to be easily replaceable.

Operation of the PPCU is similar to a baghouse operated in reverse. This allows the unit to be operated in a forced air or an induced flow system. As the contaminated flow enters the PPCU it splits, and half of it is directed to each module. Once the flow reaches a module, it enters a plenum at the bottom of the first bank or "bank A". The contaminated gas travels into the irradiated annulus between the outer quartz tube and the catalyst support. The gas is forced through the catalyst cartridge ensuring intimate contact between the contaminant and the activated catalyst. A large portion of the NG is removed in this first stage. The exact portion depends on the flow rate and initial concentration of NG. The partially treated gas exits the first bank via an exit port located above the entrance port near the top of the unit. It is transferred to the inlet of the second bank or "bank B" via external conduit. Because the banks of each module are identical, the contaminated air flows into the bottom plenum and through "bank B" in the same manner as previously described. The second stage removes the remainder of the NG. The exhaust from each module is combined into one stack and released to the atmosphere through the assist fan.

Description Summary

Equipment - A complete unit has two stand alone PPCU modules with incorporated thermal management system, one power distribution center (PDC), and one system control center (SCC). The system is designed and rated to treat 650 SCFM of annealing oven effluent. Each module may be operated independently or with the other PPCU Module in manual mode. Each PPCU Module is comprised of two banks, A and B, each containing 16 lamps. Banks can run independently or together. Main power supply for the PPCU system is fed to the PDC. The PDC also houses the communication board that controls activation of the UV lamps. All communications to and from the PDC originate from the SCC via an RS422 serial link.

Operator Interface - The PPCU operator controls the system interfacing with the SCC via local or remote terminals. The operator controls the following:

1. PPCU system with 64 lamps and thermal management system can be remotely turned on/off in Automatic mode.

2. PPCU module having 32 lamps can be turned on/off in manual mode.
3. PPCU module of 64 lamps can be turned on/off in manual mode.
4. Modules 1&2 cannot be controlled independently in Automatic mode.
5. Bank A of each module can be turned on/off in manual mode.
6. Bank B of each module can be turned on/off in manual mode.
7. Banks A and B can be controlled independently in manual mode.
8. Thermal management system can be overridden in manual mode.

Operation of PPCU System

1. Prior to start up of annealing oven cycle, PPCU and thermal management controls must be set to the automatic mode. It may be started via local interface terminal.
2. Start of the PPCU illuminates the 64 low pressure mercury lamps and activates the associated thermal management system. Four cooling fans (two per module) and four temperature controllers (one per bank) are provided. Temperature controllers provide feedback control to adjust cooling air fans based on temperature readings from four thermocouples (one per bank) inside cooling air exit cavity.
3. Cooling fans are activated by a signal from the temperature controller during lamp warm up and/or start up timer set to 15 minutes after PPCU is started. The cooling fans will provide a maximum of 150 SCFM of cooling air flow per fan.
4. After the PPCU has stabilized the operator may start the annealing oven cycle. During the annealing oven cycle, temperature sensors will monitor the exit cool air temperature. The cooling fans will run continuously and will not be toggled on and off. To maintain the cooling air exit temperature of 40-42°C, the fan blast gate may be partially opened or closed. If the temperature drifts from the desired conditions, two alarm lights located on the SCC alert the operator as follow:
 - High temperature alarm - above 60 deg C
 - Low temperature alarm - below 40 deg C
6. During the annealing oven cycle, local and remote interfaces alert the operator of lamp failures. In the event that 5% (two lamps) of module 1 or module 2 lamps fail, the operator will return to the PPCU and place the PPCU and annealing cycle in a safe condition.
7. After completion of the annealing oven cycle the operator will let the PPCU operate in an active condition for a specified time period to reactivate catalyst cartridges for a prolonged life.
8. After the post annealing period the operator may deactivate the PPCU via the local or remote terminal.

Failure Mode and Effect Analysis (FMEA)

A FMEA is a qualitative analysis which systematically postulates single event process failures (controls, components, equipment, etc.) and determines the effect of each failure mode on the subsystem/system. Identified potential and real hazards resulting from control or component failures are assigned hazard severity levels which range from Category I, Catastrophic (frequent "A"), to Category IV, Negligible (improbable "E"), see Appendix A.

This safety analytical technique is useful in identifying potentially hazardous single point failures having a high probability of occurring. A FEMA is most effective when used during the design and/or development stages of a project. This technique does not identify multiple event (simultaneous) failures which could result in equipment/facility damage, personnel injury, or other undesired event.

FEMA Summary (Refer to Appendix B)

- Gaskets and O rings - Gasket and O ring must be made of material compatible with chemicals in which they will come in contact with. Neoprene, buna rubber, and EDPM have been tested compatible with nitroglycerin (NG) and are used in solvent propellant manufacturing operations at Radford.
- Drain Plug - The drain plug will be contaminated with NG and is a potential initiation hazard when the drain plug is removed during unit cleaning. The drain plug must be made of an energy absorbing material compatible with NG and solvent. NG film, droplets, or puddles inside the PPCU must be diluted with a compatible solvent before removing the drain plug to prevent initiation during plug removal and cleaning operations.
- NG Accumulation - Operating temperature should be maintained in the PPCU for at least two hours prior to forcing warm NG laden air through the unit. Unwanted liquid NG may accumulate in the PPCU during start up if the interior is cold.
- Electrical Rating - Component failure (quartz tube breaks) will make it possible for the compartment containing UV light electrical connectors to become contaminated with explosive concentration of vapor. The air flow assist fan must also be rated to prevent ignition of solvent vapors not destroyed by the PPCU. One of the following methods must be incorporated to assure that the PPCU meets Class 1, Division 1 criteria for UV lamps, connectors, and fan:
 1. Explosion proof - ANSI/UL 1203
 2. Intrinsically safe (2 - fault) - ANSI/UL 913
 3. Purged/Pressurized (Type X or Y) - ANSI/NFPA 496.

- Quartz Sleeve - Provisions must be made to better secure the quartz sleeve to prevent it from free falling ≈ 15 inches and impacting neat NG, if present, should the sleeve come loose from the holder. Presently, the quartz sleeves are only secured with two compressed O rings.
- Assist fan - An exhaust fan is planned to be added to the operation to assist in drawing vapor through the PPCU. The assist fan will be located at the end of the PPCU drawing contaminated NG laden air through duct and PPCU. With time, NG condensate may accumulate in the fan housing. The assist fan housing must be equipped with a clean out port and a compatible plastic drain plug. Also, instructions (procedures) must be provided to make it mandatory to clean inside the exhaust fan housing routinely.

Risk Analysis

The quantitative risk analysis, presented in Table 1, determined that the overall probability of a hazardous event during normal or abnormal operation of the PPCU is an unacceptable $1.0\text{E-}3/\text{h}$. No catastrophic failures were identified. This unacceptably high risk results from the use of non-rated electrical equipment in a process environment that contains solvent vapors. Since the propellant tested at NSWC is solventless, the equipment is only exposed to NG vapors, which are destroyed prior to entering the assist fan if the unit is functioning properly. This would not be the case at RFAAP, where the unit would be exposed to ethanol, acetone, and NG vapors or fumes, some of which are unaffected by the PPCU. Elimination of non-rated equipment reduces the overall risk to an acceptable $2.5\text{E-}7/\text{h}$ for a Category 2 (critical) event. Probabilities used in the RA are documented in Appendix D.

Other hazards identified in the FMEA which were risk assessed in the Risk Analysis relate to maintenance of the unit. Replacement of bulbs or quartz sleeves and cleaning of the unit in the presence of NG condensate can result in serious operator injury and major equipment damage. The presence of NG condensate inside the PPCU is dependent on the internal temperature of the unit and the operational status of the PPCU. NG condensate may be present in the PPCU if either the cloth sleeve coated with TiO_2 is removed, torn, or not placed over the UV light, or if a UV light is burned out and goes unnoticed. Both events have a probability of $1.0\text{E-}3/\text{h}$. Failure to install o-rings or the installation of defective o-rings can also allow the quartz sleeve to fall and impact the stainless steel bottom of the cubicle. Failure of o-rings and/or bulbs while the unattended unit is operational can result in contamination of the unit in unexpected areas susceptible to initiation during maintenance or cleaning. In addition to holding the quartz sleeve in place, the o-rings prevent contamination in an electrical compartment directly above the cubicle. Positive air pressure supplied by the cooling fans also minimizes contamination in the electrical compartment. All abnormal conditions observed by the operator or maintenance personnel must be treated with extreme caution. Operating/maintenance procedures must include instruction to safely deal with these types of situations (e.g., de-

energize unit and dilute/desensitize affected area with triacetin or acetone prior to cleaning or removal).

Removal of dropping of the plastic drain plug in the bottom of the unit can result in a marginal event (category 3) if minimal quantities of NG condensate (droplets) or film are present. A safety margin analysis adjusted to the 95% confidence level was used to determine the probability of initiation for the frictional event. The impact energy was approximated using a 1 ounce weight dropped 15 inches onto steel with a contact area of 0.1-in². The probability of a marginal event was determined to be 2.1E-8/h.

One event was identified which could result in a spill. The event requires the presence of NG condensate and the operator to fail to use or replace a catch pan in the bottom of the unit. The probability of a spill during PPCU operation is 1.0E-6/h.

An additional safety concern identified during the risk analysis is the potential for NG soaked sleeves. The sleeves are an impregnated cotton, which can absorb NG if photocatalytic destruction does not occur (undetected bulb failure) during continuous operation. A previous hazards study performed at RFAAP determined that selected materials containing < 9% absorbed NG by weight are acceptably safe to handle.¹ Sleeves should be checked periodically to ensure little or no NG is being absorbed into the sleeves. If sufficient levels are detected, a change out frequency must be developed and implemented.

¹ Gabbert, J.M., "Reactivity of Selected Materials Contaminated with High Levels of Nitroglycerin," Alliant Techsystems, Inc., Radford Army Ammunition Plant, Radford, VA, Hazards Analysis Memorandum HI-93-M-007, dated March 16, 1993.

Table 1
Risk Analysis Of Photocatalytic Pollution Control Unit

SYSTEM: Solvent Recovery/Forced Air Dry										PAGE 1 OF 1		DATE: August 28, 1998			
ENGINEERING ANALYSIS										PROBABILITIES				Hazard Category	
Operation	Units of Analysis	Material of Constr.	Combust.	Process Potential	Material Response	Safety Margin	Frequency (Yr)	Event (Ep)*	Material Present (Gp)	Initiation (Ip)*	Sustained Burning (Sp)	Fire (Fp)	Transition (Tp)		Explosion (Xp)
I. PPCU															
A. Impact															
1. Operator drops quartz sleeve onto bottom of PPCU while replacing bulb	9-lb/m2	glass/steel	NG	>2.1	2.1	None	4.4E-2	1.0E-3	1.0E-3	1	1	4.4E-8	1	4.4E-8	2C
2. Quartz sleeve impacts bottom of PPCU	9-lb/m2	glass/steel	NG	>2.1	2.1	None	1	2.0E-7	1.0E-3	1	1	2.0E-8	1	2.0E-8	2D
a. O-ring failure							9.5E-2	1.0E-3	1.0E-3	1	1	9.5E-8	1	9.5E-8	2D
b. Operator leaves o-ring out, or installs damaged o-ring															
3. Plastic drain plug dropped onto bottom of unit	9-lb/m2	plastic/steel	NG	0.8	2.1	2.5	3.0E-3	1	1.0E-3	7.0E-3	1	2.1E-8	1	2.1E-8	3E
B. Friction															
1. Plastic drain plug unscrewed	psi @ 5ps	teflon/steel	NG	7,400@1	25,400 @ 3	P=2.4 V=3	3.0E-3	1	1.0E-3	6.0E-3	1	<1.0E-10	1	<1.0E-10	3E
C. Thermal															
1. NG Vapors ignited by spark in non-rated electrical equipment															
a. Foreign material breaks quartz sleeve	°C	N/A	NG	>190°C	190°C	None	1	1.0E-10	1	1	1	1.0E-10	1	1.0E-10	3E
b. O-ring left out							9.5E-2	1.0E-6	1	1	1	9.5E-8	1	9.5E-8	2C
c. O-ring failure							1	4.0E-14	1	1	1	<1.0E-10	1	<1.0E-10	2E
2. NG/Solvent vapors are ignited by non-rated assist fan	°C	N/A	NG/ Acetone	>190°C	190°C	None	1	1	1.0E-3	1	1	1.0E-3	1	1.0E-3	2B
D. Spill															
1. Catch pan not provided	N/A	N/A	NG/ Solvent	N/A	N/A	N/A	1	1.0E-3	1.0E-3	1	1	1.0E-6	1	1.0E-6	4C

*probability of an event per hour of operation

APPENDIX A

Continued

FREQUENCY DEFINITIONS

Definitions	Frequency	Definition
Frequent	A	Expected to occur frequently ($x \geq 10^{-1}$ [10^{-3}]) ³ .
Probable	B	Will occur several times in the life of a process (10^{-1} [10^{-3}] > $x \geq 10^{-2}$ [10^{-4}]).
Occasional	C	Likely to occur some time in the life of a process (10^{-2} [10^{-4}] > $x \geq 10^{-3}$ [10^{-5}]).
Remote	D	Unlikely, but possible to occur in the life of a process (10^{-3} [10^{-5}] > $x \geq 10^{-6}$ [10^{-6}]).
Improbable	E	So unlikely, it can be assumed occurrence may not be experienced (10^{-6} [10^{-6}] > x).

- AES 5
Paragraph

7.4 When attended operations are performed, hazard analysis shall show that the risk assessment (Appendix A) does not exceed 1E, 2E, 3D, or 4A.

7.5 When operations are performed where personnel are not in jeopardy, hazard analysis shall show that the risk assessment (Appendix A) does not exceed 1D, 2C, 3B, or 4A.

³ (Example of quantitative criteria per operation [per hour])

APPENDIX B - PRELIMINARY HAZARDS ANALYSIS

Failure Mode and Effect Analysis of 650 SCEM Photocatalytic Pollution Control Unit (PPCU)

Line No.	Item	Failure Mode	Failure Cause	Potential Effects	Design Safety	Hazard Category	Recommendations
1	PPCU/Exterior Housing	Gasket fails.	Unsuitable/ non-compatible gasket material used.	NG contaminated air escapes reaction chamber and NG condenses outside PPCU.	Gasket material is 1/4 inch thick neoprene which is compatible and suitable.	4C	Safety design is adequate. Recommendation: Inspect and replace deteriorated gasket during preventative maintenance. (M)
2		Ignition of NG when removing drain plug.	Drain plug threads become contaminated and sufficient energy is present to ignite NG.	NG ignites during plug removal.	Drain plug is made of an energy absorbing plastic material.	3E	Safety design is adequate. Recommendation: Dilute NG with compatible solvent before drain plug is removed. (M)
3		NG spill	Catch pan not provided under drain outlet.	NG/solvent mixture contaminates ground.	No drain catch pan present during on site review.	4C	Recommendation: Provide a catch pan under drain outlet. (M)
4		NG condenses on cold interior of housing and ducts during cold seasons.	PPCU not insulated or preconditioned (warm) before directing NG laden air through unit.	Excessive liquid NG deposits inside PPCU.	No preheating of PPCU found in operating description and no insulation noted on drawings	4E	Recommendation: Insulate PPCU including duct work. Turn on PPCU and maintain operating temperature for two hours prior to forcing warm NG laden air through unit. (M)
5	PPCU/ UV lamps	Electric spark causes initiation.	Quartz sleeve breaks and allows NG laden air into chamber containing UV lamp connections.	Ignition of NG/Air in flammable range.	UV lamp enclosure is not rated for Class 1 Division 1 hazardous locations.	2C ²	Recommendation: incorporate any one of the following methods to assure that the PPCU meets Class 1 Division 1 criteria for UV lamps, connectors, and air flow assist fan: 1. Explosion proof - ANSI/UL 1203 2. Intrinsically safe (2 - fault) - ANSI/UL 913 3. Purged/Pressurized (Type X or Y) - ANSI/NFPA 496. (M)

(M) = Mandatory (S) = Suggested

APPENDIX B - PRELIMINARY HAZARDS ANALYSIS (cont)
Failure Mode and Effect Analysis of 650 SCFM Photocatalytic Pollution Control Unit (PPCU)

Line No.	Item	Failure Mode	Failure Cause	Potential Effects	Design Safety	Hazard ¹	Category	Recommendations
6	PPCU/ Quartz sleeve	Ignition of NG from impact of quartz sleeve on bottom of PPCU.	O rings fail to secure quartz sleeve in place.	Explosive reaction when quartz sleeve impacts neat NG	Design does not include a positive securing device for the quartz sleeve.	2D ³		Recommendation: Provide positive device to secure quartz sleeve and prevent it from free falling ≈ 15 inches and impacting neat NG should the sleeve come loose. (M)
7	PPCU/ Cooling fan	Foreign material breaks quartz tube.	Foreign material can be drawn into the cooling fan and propelled into the quartz sleeve.	A broken quartz sleeve could permit contaminated air to enter the non rated area of the unit housing electrical connections.	Design includes a filter to prevent foreign material from entering the unit. Positive pressure reduces the possibility of contamination.	3E		Safety design is adequate.
8	PPCU/ Assist fan	NG/solvent vapor present and ignites from friction of impeller against metal or from an electrical spark or short	NG condensate permitted to build up in fan housing and equipment failure.	Explosive reaction	Assist fan did not have wash out port and drain outlet when reviewed onsite. Assist fan not rated for Class 1, Division 1.	2B ⁴		If the assist fan is located at the end of the PPCU drawing potentially contaminated NG laden air through it, with time NG will accumulate in the housing. Recommendation: install a clean out port and a drain opening equipped with a plastic plug in the exhaust fan housing. Provide mandatory procedure instructions to clean inside the exhaust fan housing routinely. (M)

(M) = Mandatory (S) = Suggested

¹ Hazards Severity definitions are in Appendix A.

² Hazards severity is reduced to 2E if provisions are made for Class 1 Division 1 electrical rating.

³ Hazards severity is reduced to 2E if a positive securing/retaining device is provided for each quartz sleeve.

⁴ Hazards severity is reduced to 2E if clean out ports are provided and mandatory procedures are in place to clean inside exhaust fan housing routinely.

Appendix C
Sensitivity Characteristics of Nitroglycerin (NG) and NG/Solvent Mixtures

Sample Designation	State	%TV	Threshold Initiation Level ¹				Comments
			Impact ²		Electrostatic ⁴		
			Thickness (mils)	Drop Ht (cm)	Friction ³ (lbs/fps)	Discharge (joules)	
100% NG	liquid	unknown	6	3.5	75 / 3	Sensitivity Lab No. YA-02 (standard steel test components)	
		0.67 H ₂ O	6	51		Sensitivity Lab No. YA-05 (standard steel test components)	
		0.13 H ₂ O	6	33	42 / 3	0.064	
		< 0.45 H ₂ O	6	≥ 120	≥ 470 / 8		
NG/Solvent Mixtures							
NG / Dipropylene Glycol 75/25		0.3 to 0.32	6	51	≥ 310 / 8	0.065	
NG/Diacetone Alcohol 75/25		0.16	6	100	≥ 310 / 8		
NG/DEG 75/25		0.36 to 0.54	6	64	≥ 310 / 8	0.065	

1/ Threshold initiation level is defined as the level above which initiation can occur as established by 20 consecutive failures obtained at the indicated level. Sample initiation was evidenced by LIRA infrared sensing device which detects the presence of N₂O, NO₂, CO, and CO₂ gases in sample decomposition products.

2/ Modified Bureau of Mines Test Machine - 2 Kg falling weight

3/ ABL Sliding Friction Machine

4/ Electrostatic Discharge Test - Modified Bureau of Mines test in which selective capacitors are charged at a constant 5,000 volts and discharged through a variable air gap.

Appendix D

Probabilities per hour of operation used in the Table 1 Risk Analysis

Item	Frequency (f)	Event probability (E_p)	Material Present (C_p)
A.1	4.4E-2 32 lights per unit (2 banks of 16 each unit) replaced once per month (728 hr continuous operation)	1.0E-3 Operator drops light	1.0E-3 No TiO_2 sleeve installed, or operator fails to notice burned out bulb
A.2.a	1 Continuous operation	2.0E-7 Failure of single o-ring. Assumes the remaining undamaged o-ring is unable to support the weight of the sleeve	1.0E-3 No TiO_2 sleeve installed, or operator fails to notice burned out bulb
A.2.b	9.5E-2 2 o-rings per light, 32 lights, replaced monthly	1.0E-3 No o-ring installed, or damaged o-ring installed	1.0E-3 No TiO_2 sleeve installed, or operator fails to notice burned out bulb
A.3	3.0E-3 2 drain plugs removed monthly for cleaning	1 Removal for cleaning a normal event	1.0E-3 No TiO_2 sleeve installed, or operator fails to notice burned out bulb
B.1	3.0E-3 2 drain plugs removed monthly for cleaning	1 Removal for cleaning normal event	1.0E-3 No TiO_2 sleeve installed, or operator fails to notice burned out bulb
C.1.a	1 Continuous operation	1.0E-10 Presence of foreign material (1.0E-4) and rupture of filter (1.0E-6)	1 Material normally present at potential failure site
C.1.b	9.5E-2 2 o-rings per light, 32 lights per unit, replaced monthly	1.0E-6 Requires absence of both o-rings	1 Material normally present at potential failure site
C.1.c	1 Continuous operation	4.0E-14 Failure of both o-rings simultaneously before contamination can occur (2.0E-7 each)	1 Material normally present at potential failure site
C.2	1 Continuous operation	1 Sparking is common with non-rated electrical equipment	1.0E-3 No TiO_2 sleeve installed, or operator fails to notice burned out bulb
D.1	1 Continuous operation	1.0E-3 No catch pan present	1.0E-3 No TiO_2 sleeve installed, or operator fails to notice burned out bulb

Acronyms and Abbreviations

CEM	continuous emission monitor
CERL	U.S. Army Construction Engineering Research Laboratory
COTS	commercial off-the-shelf
DoD	Department of Defense
DRE	destruction removal efficiencies
EPA	U.S. Environmental Protection Agency
ESTCP	Environmental Security Technology Certification Program
FAD	forced air dry
FSEC	Florida Solar Energy Research
FY	fiscal year
LPML	low pressure mercury lamps
NG	nitroglycerine
NJIT	New Jersey Institute of Technology
PBMA	Production Base Modernization Activity
PDC	power distribution center
PPCU	photocatalytic pollution control unit
RAAP	Radford Army Ammunition Plant
UV	ultraviolet
VDEQ	Virginia Department of Environmental Quality
VLE	vapor-liquid equilibrium
VOCs	volatile organic compounds

CERL DISTRIBUTION

Chief of Engineers

ATTN: CEHEC-IM-LH (2)
ATTN: CEHEC-IM-LP (2)
ATTN: CECC-R
ATTN: CEMP
ATTN: CERD-L
ATTN: CERD-M

U.S. Army Industrial Operations Command
ATTN: AMSIO-IBR 61299-6000

U.S. Army Environmental Center 21010-5401
ATTN: SFIM-AEC

Radford Army Ammunition Plant
Radford, VA 24141-0298

Defense Tech Info Center 22304
ATTN: DTIC-O (2)

13
6/99